Chapter-8

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List of Research Papers Published/Accepted/ Communicated

List of Publications

[1]. Vijay Kumar, Vinay Kumar Singh, Abhinav Srivastava, Gokul Nath Agrawal, "Low Temperature Synthesis of High Alumina Cements by Gel-Trapped Co-Precipitation Process and Their Implementation as Castables", ***Journal of the American Ceramic Society***, **95**[12], 3769–3775 (2012). DOI: 10.1111/j.1551-2916.2012.05453.x

[2]. Vijay Kumar, Vinay Kumar Singh, Abhinav Srivastava, "Low Temperature Synthesis of High Alumina Cements by Novel Co-Melting Precursors and their implementation as Castables with some micro fine additives", ***Journal of the American Ceramic Society***, **96**[7], 2124–2131 (2013). DOI: 10.1111/jace.12403

[3]. Vijay Kumar, Vinay Kumar Singh, Abhinav Srivastava, P Hemanth Kumar, "Auto-combustion processed high alumina cement and its implementation as bauxite based low cement castables", ***Ceramics International***, 40, 16767–16777, (2014). DOI: 10.1016/j.ceramint.2014.08. 046

[4]. Vijay Kumar, Abhinav Srivastava, V. K. Singh, **"**An Overview on High Alumina Cement as Castable Bonding Systems over Past Decade", ***The Indian Journal of research Anvikshiki***, **6**(2), 63–71, (2012).

[5]. Vijay Kumar, Vinay Kumar Singh, Abhinav Srivastava, P Hemanth Kumar, "Mechanochemically synthesized high alumina cement and their implementation as low cement castables with some micro-fine additives", ***Journal of Asian Ceramic Society***, 3 (2015) 92–102. DOI: 10.1016/ j.jascer.2014.11.004

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Low Temperature Synthesis of High Alumina Cements by Gel-Trapped Co-Precipitation Process and Their Implementation as Castables

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Use of high alumina cement (HAC) as low cement castables (LCC) and ultra-cement castables (ULCC) has increased for refractories applications over the last few years. HAC is being prepared commercially, by fusing or sintering a mixture of argillaceous and calcareous materials above 1500°C and subsequent grinding to obtain a fine powder. Powders produced by this method have low specific surface area. Therefore, the present work was aimed to prepare nano structured HAC powders at lower temperatures than the conventional one. The powder process adopted here was modified gel-trapped precipitation method as described earlier. Two compositions of calcium aluminate powders containing 70 and 80 wt% Al_2O_3, respectively, were selected. The remaining material was CaO in both mixtures. The gel powders obtained by the abovementioned process were calcined at different temperatures with varying soaking periods. The prepared cements were characterized for structural, mechanical, and cementing properties. Finally, the calcination temperature and time were optimized to obtain the desired phases in HAC. The prime cementing phases observed were CA, CA_2, CA_6, C_3A_5, and $C_4A_3SO_4$. These cements were then used with bauxite of different grain sizes to prepare LCC and then their physical properties were studied. The XRD patterns of the bauxite-based castables indicated the formation of the corundum phase along with a mullite phase in all samples. Castable containing HAC and 10 wt% zirconia substituted for bauxite improved physico-mechanical and refractory properties. Mullite formed at high temperature acts as a bonding phase and is accounted for high CCS values. These excellent properties of such castables may enable their use in various applications such as refractory lining for fabrication of steel, aluminum, copper, glass, cement, chemicals, and ceramics.

I. Introduction

High alumina cements (HACs) or calcium aluminate cements (CACs) are the only options as a refractory cement due to their high refractoriness and are suitable for high temperature applications.[1] Their hydraulic strength development is due to water bonding reactions of the calcium aluminates to form water-resistant hydrated phases.[2,3] It is a cold hydraulic bonding system. The alumina content in high-performance HAC exceeds 70% and the remaining is mainly CaO content.[4] High-performance concretes are possible from CACs and also, ultra-high strength concretes have been proposed.[5] The flexural strength of macro-defect-free concrete samples based on HAC show much higher values.[6] The difference in refractoriness between HAC and Portland cement is due to the presence of C_2S and C_3S as its main constituents of Ordinary Portland Cement (OPC), which have low eutectic points. On the other hand, HAC with high Al_2O_3 (low CaO and SiO_2), possesses a higher melting point and is used as refractory cement. CA, CA_2, CA_6, and $C_{12}A_7$ are the main constituents in HAC.[7] In addition to CA ($CaAl_2O_4$), the HAC contains major amounts of CA_2 ($CaAl_4O_7$), $C_{12}A_7$ ($Ca_{12}Al_{14}O_{33}$) phases and minor amount of un-reacted alumina. Very little amount of amounts of C_3A ($Ca_3Al_2O_6$) are observed when samples are heated above 1500°C. The amount of the Ca-rich phase $C_{12}A_7$ is found to decrease with time as it reacts with alumina to form CA_2 or CA and the amount of CA_2 formed decreases comparatively slowly with time.[8]

High alumina cement is used as binding material for monolithic applications and a significant advancement in monolithic technology is the development of refractory concretes or castables. Castables are complex refractory formulations, requiring high-quality precision-sized aggregates, modifying fillers, binders, and additives. The use of reduced cement contents in monolithic such as low cement castables (LCCs) and ultralow cement castables (ULCCs) has grown significantly over the past 10 yr. They may be cast in molds to form specific products (precast shapes) or cast "in place," as when forming a lining for a kiln furnace. The main technical advantages of LCCs and ULCCs are their excellent physical properties, such as high density, low porosity, high cold/hot strengths, high abrasion, and corrosion resistance.[9] The working life of HAC in steelmaking and other ceramic industries is greatly dependent on the material's ability to withstand high temperatures without undergoing significant deformation and corrosion.[10] Therefore, one of the approaches used throughout the later decades is to improve the performance of HAC by reduction of the liquid content formed at elevated temperatures on high-alumina refractory castables.[11] Low-melting point eutectic phases are often formed in these castables because of the reaction between Al_2O_3, SiO_2, and CaO. Outstanding gains in refractoriness have been obtained through the reduction of CaO, SiO_2, and increasing the Al_2O_3 content in HAC.[1]

Conventionally, HACs are obtained by fusing or sintering a mixture of suitable proportions of aluminous and calcareous materials such as CaO or $CaCO_3$ and alumina (Al_2O_3) at temperatures above 1500°C and subsequent grinding. The resultant product is a fine powder and typically has very low specific surface area (<1 m^2/g).[12,13] The completion of such reactions depends on the particle size, specific surface area, and the mixing of the reactant powders. Even after repeated firing grinding cycles to eliminate all of the unreacted materials, the product batch frequently contains undesirable $CaAl_4O_7$, $Ca_{12}Al_{14}O_{33}$, and unreacted starting materials. Calcium aluminate powders prepared by chemical processing techniques proved to be X-ray amorphous and of high surface area when calcined at low temperatures.[14] Parr[15] prepared $CaAl_2O_4$ by evaporative decomposition of a solution made from calcium and aluminum nitrate precursors. After heat treatment at 900°C for less than 1 h, crystalline $CaAl_2O_4$ was obtained. Therefore, the present work was aimed to prepare calcium aluminate powders through the chemical route. Combined gelation-precipitation process as

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reported earlier[16] was employed to prepare HAC. A modified sol–gel process has been developed to prepare nano structured spinel [$MgAl_2O_4$], Al_2O_3, ZrO_2, and their composite materials. This process controls the shape and size of the powders with narrow particle size distribution. High reactivity of powders is obtained with better homogeneity and purity. The conventional process for preparing HAC is carried out at around 1600°C and needs ball milling for a longer duration to reduce the particle size to submicrometer level,[17,18] but the gel powders prepared in this manner were calcined at lower temperatures for various soaking periods. The gel powders as well as the calcined cement powders were characterized for their different physical properties and phases. The results of the present work show the formation of desired phases between 1200°C and 1350°C for a maximum soaking period of 180 min. The prime cementing phases observed were mainly CA, CA_2, CA_6, C_3A_5, and $C_4A_3SO_4$. The calcium sulfo-aluminate phase ($C_4A_3SO_4$) is quick setting and gives the initial strength.[19] This constituent, calcium sulfo-aluminate or $C_4A_3SO_4$, has been known as a cementing phase for many decades.

Further, HACs thus prepared by gelation and precipitation method were used to prepare LCCs. To this end, refractory grade of high alumina containing bauxite of different grain sizes were selected as aggregates. First, the packing density of samples was optimized by selecting different fractions of aggregates and the best batch of composition was then selected to give maximum packing density. These castable samples were further studied for their thermo-mechanical and structural properties. The bauxite matrix was also partially replaced by micro-fine ZrO_2 and its effect on physical properties of castables was observed. The experimental results were also compared with the standard commercial existing HAC from Almatis (Kolkata, India) (code name CA-14M with 70% Al_2O_3 and CA-25 C with 80% Al_2O_3).

II. Experimental Procedure

(1) Material Characterization

The starting raw materials A.R. grade aluminum sulfate, calcium carbonate, and ammonia solution were supplied by Fisher Scientific (Mumbai, India).

(2) HAC Powder Preparation

Aluminum sulfate lends itself easily to gel formation and is a low cost material. The solution of aluminum sulfate easily reacts with NH_4OH and forms aluminum hydroxide. Proper selection of molarity and simultaneous stirring gives it a gel-like structure. It was therefore decided to use it with calcium carbonate as starting raw materials to prepare HAC through a composite gel process. In this system, clear solution of aluminum sulfate of 0.3*M* was obtained by dissolving the salts in distilled water with simultaneous magnetic stirring and subsequent filtering. For complete dissolution of the salt, the solution was kept on a hot plate at around 60°C with simultaneous stirring. Solutions having concentrations of 0.3*M* were prepared in this manner. $CaCO_3$ was mixed in double distilled water to obtain a suspension of $CaCO_3$ having 50 wt.% mass. This suspension was then mixed in aluminum sulfate solution to give a final 7:3 and 8:2 Al_2O_3/CaO molar ratio. For the preparation of the gel, ammonia solution was added dropwise from a beaker into mixed solutions of aluminum sulfate and calcium carbonate with continuous magnetic stirring. A point was reached when the gel became fully viscous and the process of stirring was stopped due to the viscous nature of the gel. The gel obtained in this process was the composite of aluminum hydroxide, aluminum sulfate, and calcium carbonate because at this concentration some amount of aluminum sulfate remained unreacted and was trapped within the hydroxide gel network.[20–24] The prepared gel was air dried in an oven at 80°C to complete dryness. The dried gel powders were calcined at varying temperatures ranging from 1200°C to 1350°C. They were kept for a 3-h soaking period in the SiC muffle furnace. The heating rate was maintained at 5°C/min.

(3) Consistency of Cement

Consistency is a measure of plasticity of a cement paste. It refers to the degree of wetness exhibited by a freshly mixed concrete, mortar, or neat cement ground whose workability is considered acceptable for the purpose at hand. It is measured as the amount of water required as to a particular wt% of dry cement which permits the Vicat's plunger of 10 mm diameter to penetrate to a point 5–7 mm from the bottom of Vicat's mold with gauging time of 3–5 min. Calcined HAC powder having 70% alumina, and 80% alumina content samples were tested for consistency by Vicat's apparatus.

(4) Setting Time Test

Calcined powders were tested for initial and final setting by Vicat's apparatus according to ASTM C403.

(A) Initial/Final setting time of HAC: This early period in the hydration and strengthening of cement is referred to as the "initial setting" of cement. The initial setting time was measured by taking 50 g of HAC mixed with the percentage of water required for normal consistency. In Vicat's apparatus, a needle is allowed to penetrate through the cement block prepared. In the initial stage, a thicker needle is allowed to pierce through the test block. This procedure is repeated till the paste starts losing its plasticity, and the penetration is limited only to 5–7 mm depth. This duration of setting is counted and is termed as the initial setting time.

(B) Final Setting of HAC: The cement shall be considered as finally set when, upon, lowering the attachment gently cover the surface of the test block, the thinner needle makes an impression. The duration of this process is considered as the final setting time.

(5) Castable Formulation

Refractory castables are generally prepared using approximately 5 wt% HAC cements as low cement castable in refractory grade of high alumina-containing bauxite and other refractory materials.[25,26] The calcined bauxite that was used in castable formulation in the present study contained approximately 70%, 18%, 3%, 4%, and 1% by weight Al_2O_3, SiO_2, Fe_2O_3, TiO_2, and alkalis, respectively, as specified by the supplier. The bauxite matrix (Bauxite Supplier, Kailash Marketing Associates, Mumbai, India) was subsequently replaced by small additions of micro-fine ZrO_2 powder. The effect of ZrO_2 addition on thermo-mechanical and structural properties was also observed. In the first step for cement castable formulation, calcined bauxite was oven dried, crushed, and grinded for grading in a planetary ball mill. The jar and grinding media were of titanium-coated steel material. At one time, 200 g of calcined bauxite material was taken in a jar and grinded in a planetary ball mill for 30 min at 500 rpm. Similarly, it was processed to complete the grinding of 3 kg material. The ground material was then kept in various selected sieves and set up on the motorized vibro-sieving equipment for grading. After separation of different graded bauxite, experiments were performed further. The particle size distribution has an important role in the properties of refractory castable. Incorrect particle size distribution may cause militancy or the excess water requirement by the castables. The particle size distribution of the fine fraction is generally a representation of the flow characteristics. The trials of aggregate proportions were taken in a 1000 cm^3 flask filled up to 250 cm^3 and vibrated for 20 s and the packing density calculations were carried out for each trial. Aggregates having highest packing densities were chosen for further analysis.

In the next step, batches were prepared by taking different grades of materials in the proper proportion. The materials were dry mixed in a plastic container for 10 min by spatula and then were taken for sample preparation. Generally, ultra and LCCs require less than 5 wt% of water to achieve the desired rheology; therefore, water was added in two steps. The casting was done by adding first two-thirds proportion of water at a time. Then, one-third of water was added slowly to get a homogenous mixing. The wet mixing was performed for up to 5–6 min to achieve proper flow. Immediately after wet mixing, the castable mix was filled into a cube (30 mm × 30 mm × 30 mm) made of hard steel. The cube was placed on the vibrating table filled with the wet mixed castable and the mixes were vibrated for 5 min, showing better compactness. For each composition, several cube samples were prepared for laboratory testing. The samples were cured in a moisture-saturated environment (95% RH) in a humidity chamber at room temperature for different time periods. For firing the samples, they were first oven dried at 110°C for 24 h. The test samples were fired at 1400°C with a variation of ±5°C in an electric SiC heating element furnace with maximum soaking time of 3 h. The cured samples as well as the fired samples were tested for bulk density, apparent porosity, and cold crushing strength (CCS). These samples were also analyzed by XRD for phases present and by SEM for their morphological behavior.

(6) *Cold Crushing Strength of HAC and LCC Formulated*

The CCS is the capacity of a material to withstand axially directed pushing forces. By definition, the compressive strength of a material is that value of uniaxial compressive strength reached when the material fails completely. CCS of cement was measured as the compressive strength of a 2.5 cm cement cube made of pure HAC (without any aggregates). These samples were tested for compressive strength after 3 h, 1 d and 2 d, respectively, according to (ASTM C1194). The castables prepared with varying compositions (bauxite aggregates and fine zirconia) were also tested for their CCS. For each composition testing, 12 cubic samples were prepared.

III. Results and Discussion

(1) *Thermal Analysis*

The dried gel powders were examined for DTA/TGA. Thermal analysis (DTA/TGA) of the dried gel was carried out in NETZSCH STA 409 (NETZSCH Technologies India Private Limited, Chennai, India) by heating the sample in an alumina crucible at 10°C/min upto 1300°C. Figures 1–3 are the DTA/TGA curves of alumina gel, calcium carbonate gel, and composite gel for HAC powders, respectively.

Figure 1 shows the DTA/TGA curve for alumina sulfate gel. Exactly 22.5 mg of dried gel was taken and heated at the rate of 10°C/min up to 1300°C. Thermal analysis of alumina gel shows the loss of the hydroxyl group and decomposition of remaining aluminum sulfate salts. Decomposition started at 80°C and ended at 800°C. At 100°C, evaporation of free water starts. At 225°C, loss of chemically combined water is completed. At 235°C–360°C, decomposition of ammonium sulfate and this peak is endothermic. Weight loss at 360°C is 22.22%. At 360°C–430°C, decomposition of aluminum hydroxide and this peak is endothermic. Weight loss at 430°C is 35.55%. At 840°C, there is 71.11% weight loss. At 400°C–800°C, decomposition of sulfates occurs. Weight loss at 580°C is 48.0%. Five endothermic peaks occur in the temperature range 300°C–900°C. All the losses occur up to 840°C and there are no remarkable changes above this temperature. Beyond 900°C there is no change in weight.

In Fig. 2, decomposition of $CaCO_3$ can be predicted around 800°C showing a great exothermal change.

Figure 3 shows the decomposition of composite gel powder, prepared to obtain HAC. 24.7 mg of dried gel was taken and heated at the rate of 10°C/min up to 1300°C. Decomposition occurs in the temperature range 80°C–1300°C. Many exothermic peaks were observed in the temperature range 1000°C–1300°C showing the formation of different phases. At 100°C, there is 8.09% weight loss. At 530°C, there is 23.48% weight loss. At 840°C, there is 36.45% weight loss.

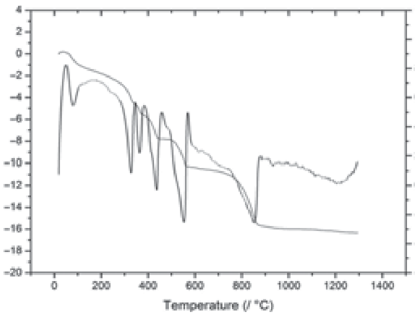

Fig. 1. DTA–TGA of alumina sulfate gel heated at the rate of 10°C/min up to 1300°C.

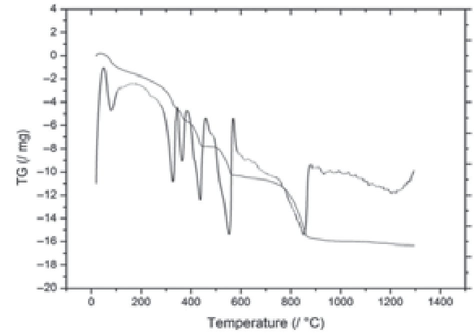

Fig. 2. DTA–TGA of $CaCO_3$ heated at the rate of 10°C/min up to 1300°C.

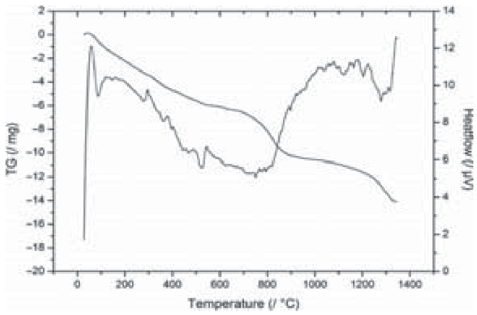

Fig. 3. DTA–TGA of Composite heated at the rate of 10°C/min up to 1300°C.

A comparison of the above three figures shows that there is less loss and low thermal effect in the composite gel powder. Results showing the exothermal peaks above 1000°C just indicate the formation of different phases in these composite gel powders.

(2) *Evolution of Phases by X-Ray Diffraction*

X-ray diffraction patterns were observed using a Rigaku portable XRD machine (Rigaku, Tokyo, Japan). Calcined sample powders were analyzed by X-ray diffraction for phases present in the fired sample. Phase identification analysis was carried out by comparing the respective powder X-ray diffraction patterns with the standard database stated by JCPDF.[27] Detailed analyses of the phase formation and changes over the temperature range and variation in compositions were carried out.

Figures 4 and 5 are the XRD patterns of samples fired at 1350°C with 70% and 80% alumina, respectively. CA_6 begins

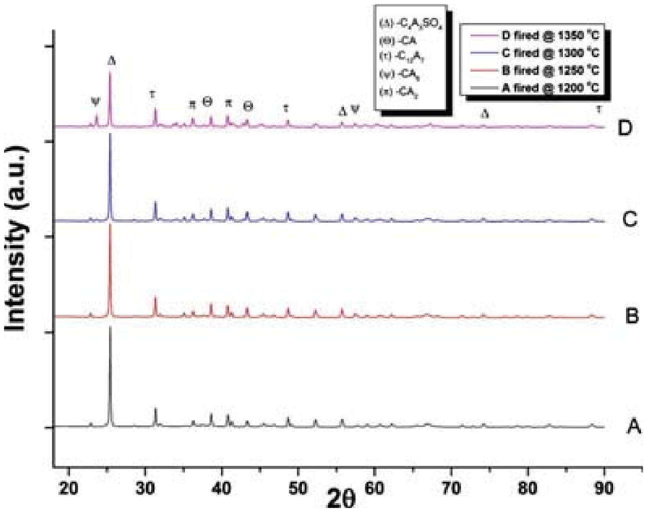

Fig. 4. XRD of HAC containing 70% Al_2O_3 fired with varying range of temperature.

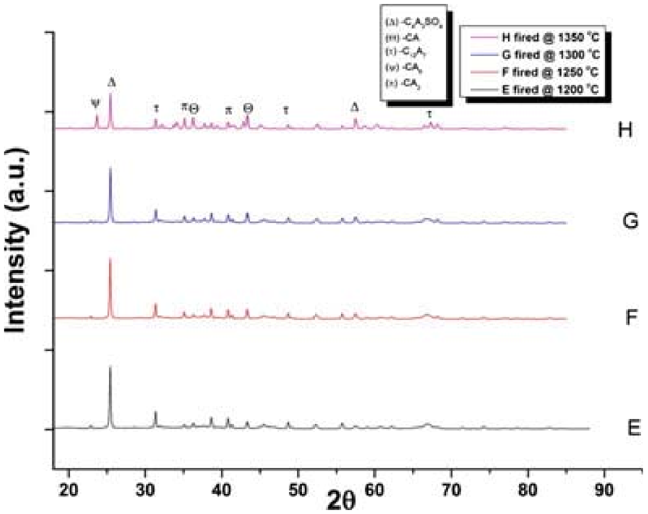

Fig. 5. XRD of HAC containing 80% Al_2O_3 fired with varying range of temperature.

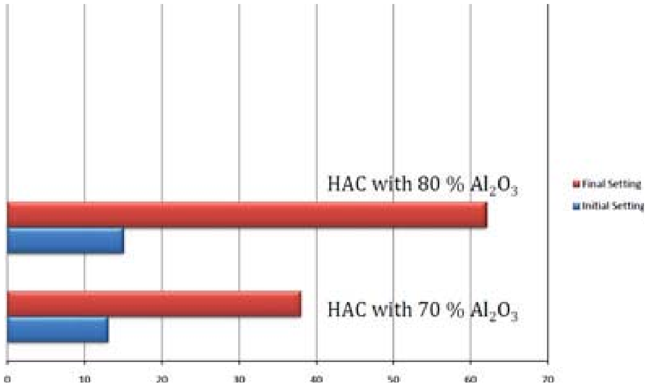

Fig. 6. Setting behavior of HAC

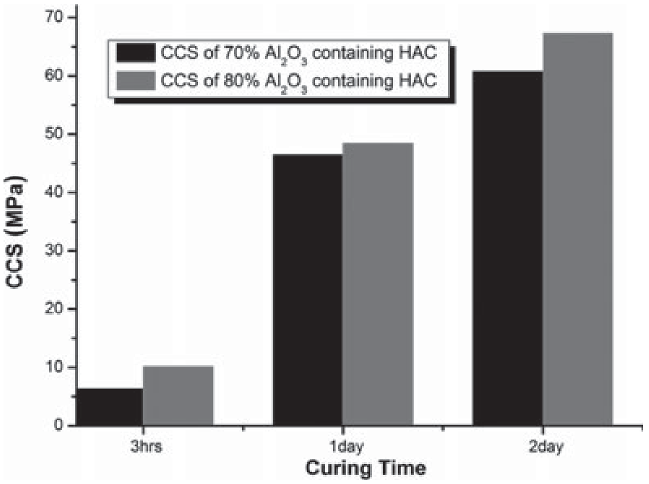

Fig. 7. Effect of curing period on CCS of HAC fired at 1350°C

to form in the temperature range starting from 1250°C in both compositions, one having 70% alumina and the other having 80% alumina. The major phase in both compositions is found to be CSA. The formation of this phase is concluded due to the presence of sulfates which remained unreacted with ammonium hydroxide. Evolution of sulfates at high temperature yields the formation of CSA. Figure 4 shows that the sample is composed mainly of mono-calcium aluminate $CaAl_2O_4$ (CA), di-calcium aluminate $CaAl_4O_7$ (CA_2), calcium sulfo-aluminate $C_4A_3SO_4$, dodecacalcium heptaaluminate $12CaO{\cdot}7Al_2O_3$ ($C_{12}A_7$), and calcium hexa-aluminate $CaAl_{12}O_{19}$ (CA_6) peaks.

Figure 5 shows the sample exhibiting some peaks characterizing CSA, CA, CA_2, and CA_6 with few amount of $C_{12}A_7$. The readily formed and thermodynamically stable phases in the CaO–Al_2O_3 binary system with increasing refractoriness in the above order could be predicted due to excess alumina content.[28,29] In the conventional preparation route by high-temperature solid-state synthesis, the batch usually contains CaO-rich phases and unreacted Al_2O_3 before the appearance of the desired product phase.[30,31]

A single-phase mono calcium aluminate was produced only after a prolonged reaction time at high temperatures in a batch that was proportioned for CA.[32,33] The formation sequence of phases in these mixtures was always from calcia-rich phases to the proportioned phase. For example, when the starting mix was prepared for CA_2 (CaO: Al_2O_3 = 1:2), initially Ca formed in large amounts which, with time and temperature, converted to CA.[34] Singh *et al.* explained this behavior by a higher reactivity of CaO with respect to Al_2O_3. Contrary to this observation, CA and CA_2 were both observed in the early stages of crystallization in chemically prepared mono calcium aluminate powders.[30]

(3) Setting Behavior of HAC

Figure 6 shows the setting behavior of HAC. The prepared HAC powders were mixed with water (0.85 P). At room temperature, 70% alumina containing cement gave an initial setting time of 13 min and final setting occurred in 38 min. Another composition of HAC having 80% alumina had an initial setting time of 15 min and a final setting time of 62 min. With increasing alumina content in HAC the setting time showed an increasing trend.

(4) CCS of HAC Fired at 1350°C

The pure (without any aggregates) HAC attained good structural strength as obtained from experimental work and shown in Fig. 7. Samples were tested after cured for 3, 24, and 48 h, respectively. The strength increased rapidly with curing time in all the compositions. Initially, in 3 h, the CCS value obtained for HAC sample having 70% alumina is 6.3 MPa and for 80% alumina it is 10.2 MPa. After 48 h it is 60.75 and 67.3 MPa for 70% and 80% alumina cement, respectively, which is better than the commercially available CA-14M-55MPa and CA-25C-50MPa (Almatis). It gets the maximum strength at around 48 h and after this period there is a very slight variation. It can be predicted that HAC samples having 80% alumina have more compressive strength than the 70% alumina sample. The higher strength of 80% alumina is ascribed to the presence of CA_2 and $C_{12}A_7$ as a major component, as it reacts rapidly with water. It is well known that CA_2 and$C_{12}A_7$ react significantly in the early ages of hydration, and the hydration of $C_{12}A_7$ is very exothermic, so the formation of stable hydrates generally occurs sooner.[1] Although CA_2 is known to react slowly with water in the early stages of hydration, its presence along with CA results in an overall faster hydration rate as the heat of hydration resulting from the hydration of CA activates CA_2 and makes it react relatively faster with water than it would do alone but not than $C_{12}A_7$.[34,35] CCS data of the sintered ceramics bodies exhibit high strength of both samples after firing. This is due to the formation of the ceramic bond.[36] The higher strength of 80% alumina-containing cement sintered at 1350°C is due to the presence of $C_{12}A_7$ and CA_6, which has low melting eutectic point as shown in the phase diagram of $CaO\text{-}Al_2O_3$.[1] This low melting phase led to a decrease in porosity and an increase in mechanical properties.[37]

(5) Soundness of HAC Fired at 1350°C

The HAC samples were tested for soundness by the Le Chatelier method to find out the expansion. The expansion was 1.3% in an HAC sample having 70% alumina and 1.0% in an HAC sample having 80% alumina content.

(6) Scanning Electron Microscopy (SEM) of Formulated Castables

Broken pieces of formulated castable were examined using a FEI Inspect S-50 (FEI ASIA PACIFIC, Shanghai, China) scanning electron microscope. The samples were metalized by gold sputtering for better image definition. Figure 8(a) shows SEM micrographs of a hydrated HAC sample containing 80 wt% Al_2O_3 (numbers 1–4 in the figure show their magnification). Networks of well-crystallized interlocking hexagonal plates of CAH_{10} andC_2AH_8 can be observed in Fig 8(a). The phases known to be the main hydration products of CA, CA_2, and $C_{12}A_7$ play a bonding role in such materials. The higher C/A ratio of $C_{12}A_7$ favors the formation of C_2AH_8 and very little CAH_{10}. Figure 8(b) shows SEM micrographs of a castable at different locations and magnifications. The microstructure of the castable in Fig 8(b) shows a highly homogenous formation of corundum and mullite after firing the castables prepared at 1400°C. This firing leads to dense body formation. Coarse particles of corundum are observed to be embedded in the bed of finer needle-shaped particles of mullite. This shows the uniform packing of bauxite matrix due to proper grain bonding. The same could be observed with different magnification levels (numbered 1–4) with more clear aspects. The average particle size deduced from this micrograph is in the range of 10–20 μm.

(7) XRD Patterns of Castables Fired at 1400°C for 3 h

Figure 9(a) shows the XRD pattern of LCC prepared with 70% Al_2O_3 containing HAC and Fig. 9(b) shows the XRD pattern of LCC prepared with 80% Al_2O_3 containing HAC. Here, Y_0, Y_5, and Y_{10} indicate the content of 0%, 5%, and 10% zirconia, respectively, introduced in the bauxite matrix with a constant 5% weight of 70% alumina containing HAC. Similarly, Z_0, Z_5, and Z_{10} are the one with 80% alumina containing HAC. The corundum phase appeared due to the transformation of bauxite minerals to corundum. The presence of different impurities in bauxite versus alumina helps the formation of the mullite phase that appeared as a result of the reaction between silica impurities and alumina in the castable samples sintered at 1400°C for 3 h.

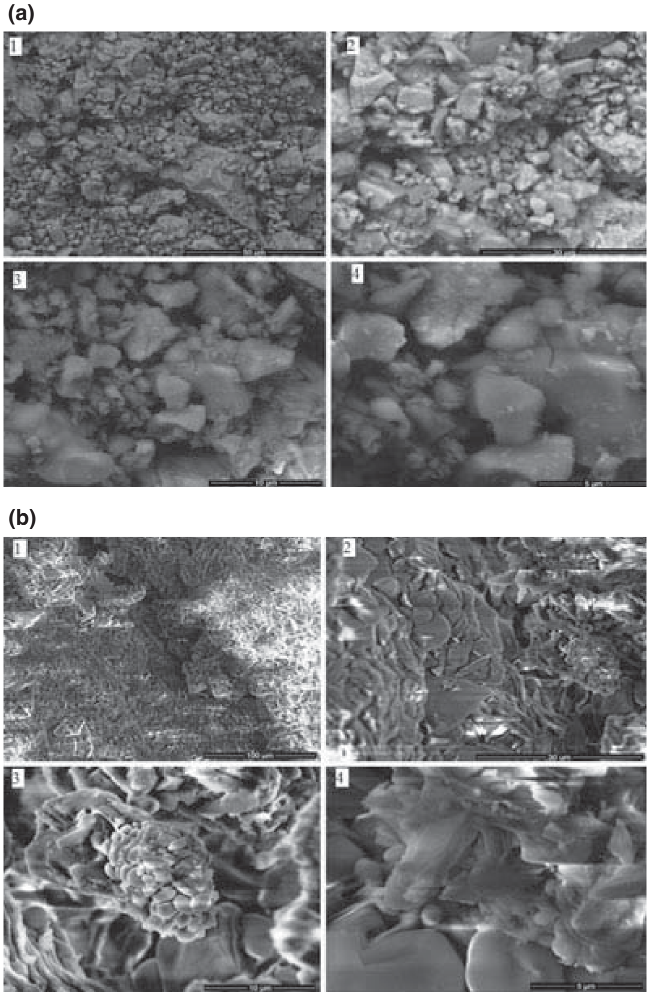

Fig. 8. (a) SEM of hydrated HAC containing 80% Al_2O_3 with different magnifications. Figures with numbers 1, 2, 3, and 4 represent their magnifications, viz., 2500×, 5000×, 10 000× and 20 000×, respectively. (b) SEM of the LCC prepared by HAC containing 80% Al_2O_3 with different magnifications. Figures with numbers 1, 2, 3, and 4 represent their magnifications, viz., 1000×, 5000×, 10 000×, and 20 000×, respectively.

(8) Bulk Density and Apparent Porosity

In the castables prepared, highest average bulk density is achieved at around 2.82 g/cm^3 for the compositions having 10 wt% zirconia. This can be attributed to the use of higher percentages of alumina and micro-fine zirconia in the aggregate. Apparent Porosity was measured to be around 9% in the castables prepared with 10 wt% of zirconia. All these tests were performed on LCC prepared with 80% Al_2O_3 containing HAC.

(9) CCS of Different Castable Compositions Fired at 1400°C for 3 h

Prepared HAC was used as addition on LCC consisted of 80–100 wt% calcined bauxite aggregate and 5 additional weight% HAC. Zirconia is substituted for bauxite by 0, 5, 10, and 15 wt%. Y and Z have same notifications and compositions as described in Section III*(7)*. CCS of the castables fired at 1400°C is shown in Fig. 10. Seventy percent alumina containing HAC castables Y0, Y5, Y10, and Y15 samples shows high values of CCS—225, 235, 280, and 260 MPa, respectively. The highest values of CCS of castables are certainly related to the formation of mullite which strengthens the structure at high temperature. When the percentage of fine particles (zirconia) increases in the castables, the CCS increased. Similarly, 80% alumina containing

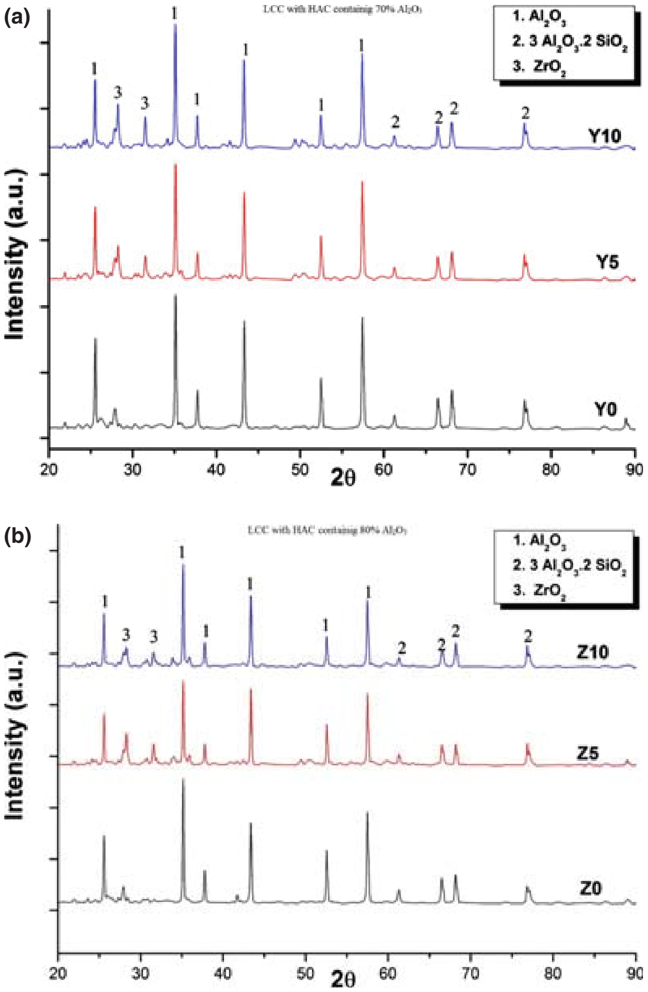

Fig. 9. XRD of castables prepared by HAC containing (a) 70% Al_2O_3 and (b) 80% Al_2O_3 fired at 1400°C.

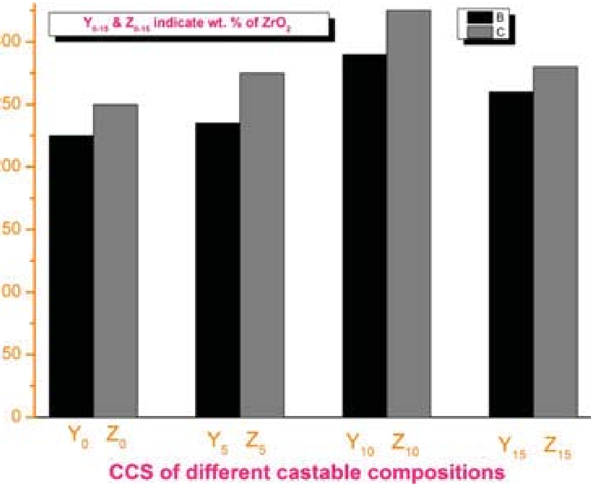

Fig. 10. CCS of different castable compositions where Y denotes HAC of 70% Al_2O_3 and Z denotes HAC of 80% Al_2O_3.

HAC castable Z0, Z5, Z10, and Z15 has CCS values of 250, 275, 325, and 290 MPa, respectively. The CCS of the HAC prepared is higher in comparison with the CCS of Secar71-160MPa and Secar80-200MPa with conventional bauxite containing LCC. The CCS of the samples of zirconia and bauxite castables is determined and shown in Fig. 10. The maximum average strength is attained in castables with 10 wt% of zirconia.

IV. Conclusion

The gel-trapped precipitation process used to prepare HACs yields fine and thermally reactive powders. Desired cementing phases having high refractoriness like CA, CA_2, $C_{12}A_7$, CA_6, and $C_4A_3SO_4$ begin to form in the temperature range of 1200°C–1350°C. This may be the possible method for the commercial preparation of HAC at lower temperatures. Cement selection was made on the basis of optimization of properties. HAC formed at 1350°C was found to be superior among all HACs that formed at varying temperature ranges. One advantage of this process is to exclude silicate phases having low eutectic temperatures in such cements. These silicate phases decrease the refractoriness and the cement cannot be used at higher temperatures. Castable samples prepared by HAC having 80% alumina have better physical and cementing properties than the HAC having 70% alumina. Although these samples have high initial and final setting time, better CCS values at different curing times were obtained. Moreover, the HAC samples attain maximum strength within 48 h. The XRD patterns of the bauxite-based castables indicate the formation of the corundum phase along with mullite phase in all samples. Castable containing 10 wt% zirconia substituted for bauxite improves physico-mechanical and refractory properties at most. Mullite formed at high temperature acts as a bonding phase and is accounted for by the high CCS values. These excellent properties of such castables enable their use in various refractory applications such as fabrication of steel, aluminum, copper, glass, cement, chemicals, and ceramics.

Acknowledgments

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Low Temperature Synthesis of High Alumina Cements by Novel Co-Melt Precursors and Their Implementation as Castables with Some Micro Fine Additives

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In the present investigations nano size high alumina cements (HAC) were prepared by very effective co-melt precursor sintering technique from their metal nitrate precursors. The prime cementing phases observed were CA, CA_2, and $C_{12}A_7$. The addition of nano structured cements in refractory castables has improved the thermo-chemical-mechanical properties to a significant extent. Each batch of low cement castables (LCC) was prepared from calcined Chinese bauxite, HAC, and superfine additives. The effect of HAC in bauxite castable with the additives similar to Silicon Carbide, reactive alumina, and micro-fine silica on the sinterability and properties of these castables was investigated. Physical properties such as apparent porosity and bulk density, mechanical properties such as hot modulus of rupture (HMOR), cold and hot modulus of rupture (CMOR), and cold crushing strength (CCS) of hydrated and sintered castables were studied. The sintered castables were also characterized for their solid phase compositions and microstructure using X-ray diffraction (XRD) and FE-SEM, respectively. In the castables new phases such as mullite, α-alumina were formed at the expense of bauxite and silica. Solid solution of mullite formed at high temperature acts as a bonding phase and is accounted for high HMOR, CMOR, and CCS values. These excellent properties of such castables may enable their uses in various applications such as refractory lining for fabrication of steel, aluminium, copper, glass, cement, chemicals, and ceramics.

I. Introduction

High alumina cement is being prepared commercially, by fusing or sintering a mixture of argillaceous and calcareous materials above 1500°C and subsequent grinding to obtain a fine powder. Enormous quantities of air pollutants are emitted from cement production, including SO_2, NO_X, CO, PM and result in significant regional and global environmental problems. To get rid of such environmental concerns a novel process is required which could not only bring down the cost of production but could also chain up the pollution norms. Low temperature synthesis of HACs by gel trapped co-precipitation process is described earlier.[1] CA, CA_2, CA_6, $C_{12}A_7$ are the main constituents of HAC. Sometimes, it also contains some minor amount of un-reacted alumina. Very little amounts of C_3A ($Ca_3Al_2O_6$) are observed, only when samples are heated above 1500°C.[2] The main use of HAC is in applications, which require substances which combine the advantages of casting at ambient temperatures with excellent performance at temperatures above 1700°C. HACs with 70–80 wt% Al_2O_3 can be used to produce castables with a temperature resistance ranging from 1800°C to 1900°C.[3] These materials are used for many special applications in the construction, civil engineering, and refractory industries because of their ability to gain strength rapidly and to withstand aggressive environments and high temperature.[4,5] The knowledge of their mechanical behavior at a young age becomes essential to forecast their performance in service. To describe hydration of cement paste at the early age (from a few minutes to a few hours after mixing), different approaches have been developed. Conductivity and pH measurements, usually carried out on dilute systems have been applied to predict the dissolution and precipitation processes.[6,7] Nano ceramic materials (<100 nm grain size) are still in the early stages of development, but depict many processing and property advantages over their conventional coarse grained alternatives. In recent years there has been increasing interest in the synthesis of nano crystalline metal oxides.[8,9] It is well-known fact that the morphology and particle size distribution are important factors that influence physico-chemical properties of materials, yet the lack of suitable, consistent, and low cost methods of preparation have limited their ability to control these factors during synthesis. In the past few decades, there was a great interest in improving the quality of refractory castable through decreasing the cement content, i.e., 4%–8% in LCC or 1%–3% in ultra-low cement castables (ULCC) or <1% in zero cement castables (ZCC). Decreasing the CaO content in these castables eliminates the disadvantages of the conventional castables (10%–20%), which inherently included high porosity, lower strength, and slow control over curing and drying processes. These were due to their higher amount of water requirement, which was a major drawback resulting in their loss of strength during the dehydration process at 500°C–1000°C.[9] Moreover, the presence of a high content of CaO in conventional castables decreases the refractory properties due to the formation of low melting compounds at high temperatures. These disadvantages have been eliminated in the new generation of high technology castables, which enables their use in a wide variety of applications.[10] These castables develop very high performance during and after heating. They are used when high thermal shock resistance or resistance against abrasion and corrosion by slag or melted metals are required.[7,9] These castables require good control during installation, i.e., rheology and hardening kinetics, which are influenced not only by the intrinsic reactivity of the calcium aluminate cement but also by the interactions between fillers and calcium aluminate cement.[11] The attraction of low cement and ULCC for refractory applications is due to their high strength, thermal shock resistance, corrosion resistance, and their economic effect derived from the use of natural bauxite resources. They have already been successfully employed in molten iron torpedo cars, blast-furnace troughs and incinerator linings and may yet acquire wider applications in high-temperature industries. Recently, a group of additives

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appeared in the refractory industry that triggered new prospects for castable producers. The additives comprise ultra-fine particles, for example silica, alumina, mullite, spinel, and carborundum. In previous investigations[12] lower amount of cement in conjunction with fine grain-sized materials having high surface area and dispersing aids were used. Those materials were silica fume, Al_2O_3, Cr_2O_3, ZrO_2, TiO_2, SiC, clay mineral, and carbon. It was concluded that the presence of such materials promote refractory properties such as volume stability and well balanced physical and hot mechanical properties. The presence of zircon with fine alumina as a filler tends to form mullite/ZrO_2 composite after firing. The formation of mullite and zirconia is of vital importance as these bonding phases exhibit high refractoriness, low creep rate, low thermal expansion, good chemical and thermal stability, and good toughness and strength.[13] Nowadays, low and ULCC containing SiC have gained wide acceptance as materials for hot metal and slag runners. Silicon carbide is being introduced to enhance the thermo mechanical properties of the composite under operating conditions. Some authors studied high-temperature strength and thermal shock of ultra and LCC in relation to their microstructure feature. These castables have been composed of SiC-containing bauxite. They found that castable specimens had significantly improved in HMOR studied at 1400°C.[14] However, the problem of SiC oxidation limits its presence in refractory castables. The aim of the present work was to synthesize a novel co-melt precursor HAC and their implementation in bauxite containing castable to investigate the sintering effect of SiC, silica fume, and reactive alumina.

II. Experimental Procedure

(1) Material Characterization

The starting A.R. grade raw materials aluminum nitrate, calcium nitrate, silica fumes, silicon carbide powder, and reactive alumina were supplied by Loba Chemie Pvt. Ltd., Mumbai India.

(2) HAC Powder Preparation

Hydrated aluminum nitrate $Al(NO_3)_3{\cdot}9H_2O$ and hydrated calcium nitrate $Ca(NO_3)_2{\cdot}4H_2O$ were weighed and mixed on a laboratory scale to give the equivalent molar ratio of 7:3 and 8:2 Al_2O_3/CaO, which were denoted as HAC70 and HAC80 HAC samples, respectively. The mixtures were heated in a porcelain dish on a hot plate at about 250°C until it melted completely, and were then air quenched. The resulting solids were heated at 500°C for 3 h. Samples of the HAC powders obtained were finally calcined at 800°C, 900°C, and 1000°C in a platinum dish using a SiC muffle furnace for soaking period of 10 min. After soaking, the powders were quenched and stored in a desiccator.

(3) Consistency of Cement

Consistency is a measure of plasticity of a cement paste. It refers to the degree of wetness exhibited by a freshly mixed concrete, mortar, or neat cement ground whose workability is considered acceptable for the purpose at hand. It is measured as the amount of water required as to a particular wt % of dry cement which permits the Vicat's plunger of 10 mm diameter to penetrate to a point 5–7 mm from the bottom of Vicat's mold with gauging time 3–5 min. Calcined HAC powder having 70% alumina and 80% alumina content samples were tested for their consistency by Vicat's apparatus.[1]

(4) Setting Time Test

Calcined powders were tested for initial and final setting by Vicat's apparatus according to ASTM C403.

(A) Initial Setting of HAC: This early period in the hydration and strengthening of cement is referred to as "initial setting" of cement. The initial setting time was measured by taking 50 g of HAC mixed with the percentage of water required for normal consistency. In Vicat's apparatus a needle is allowed to penetrate through the cement block prepared. In the initial stage, a thicker needle is allowed to pierce through the test block. This procedure is repeated until the paste starts losing its plasticity, and the penetration is limited only to 5–7 mm depth. This duration of setting it counted and termed as initial setting time.[1]

(B) Final Setting of HAC: The cement will be considered finally set when, upon, lowering the attachment gently cover the surface of the test block, the thinner needle makes an impression. The duration of this process is considered final setting time.[1]

(5) Castable Formulation

Low cement refractory castables are generally prepared using approximately 5 wt% HAC cements and refractory grade high alumina containing bauxite with certain superfine additives. The calcined Chinese bauxite that was used in castable formulation in this study contained approximately 88.60%, 4.78%, 1.58%, 4.0%, 0.26%, 0.08%, and 0.70% by weight Al_2O_3, SiO_2, Fe_2O_3, TiO_2, CaO, Na_2O, and others, respectively, as specified by the supplier. In the bauxite matrix small additions of reactive alumina, micro-fine silica, and SiC powder was made. The formulation Tables I and II show the detailed composition with their specific names. The effect of these additions on thermo-mechanical and structural properties was also observed. In the first step for cement castable formulation, calcined bauxite was oven dried, crushed, and grounded for grading into different sizes in a planetary ball mill. The jar and grinding media were of titanium-coated stainless steel material. At one time 250 g of calcined bauxite material was taken in a jar and grounded in a high-energy planetary ball mill for 45 min at 600 rpm. Similarly, it was processed to complete the grinding of complete material. The ground material was then kept in various selected sieves and set up on the motorized vibro sieving equipment for grading. After separation of different graded bauxite, experiments were performed further. Figure 1 is the pictorial representation of particle size analysis done with the help of standard Tyler mesh. The particle size distribution of the fine fraction is generally a representation of the flow characteristics. The particle size distribution has an important role in the

Table I. Batch Composition with HAC70

Sample	HAC70 (wt%)	Chinese Bauxite (wt%)	SiC (wt%)	Reactive Al_2O_3 (wt%)	Microfine SiO_2 (wt%)
R1	5	80	5	5	5
R2	5	80	5	6	4
R3	5	80	5	7	3
R4	5	80	5	8	2
R5	5	80	5	9	1
R6	5	80	5	10	0

Table II. Batch Composition with HAC80

Sample	HAC80 (wt%)	Chinese Bauxite (wt%)	SiC (wt%)	Reactive Al_2O_3 (wt%)	Microfine SiO_2 (wt%)
S1	5	80	5	5	5
S2	5	80	5	6	4
S3	5	80	5	7	3
S4	5	80	5	8	2
S5	5	80	5	9	1
S6	5	80	5	10	0

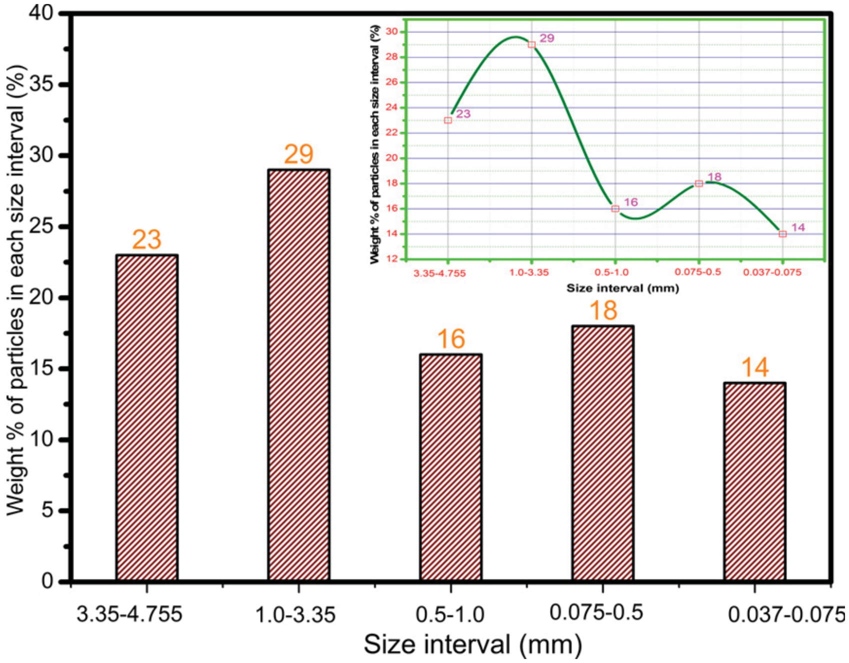


Fig. 1. Bauxite particle size.

properties of refractory castable. Incorrect particle size distribution may cause militancy or the excess water requirement by the castables. The trials of aggregate proportions were taken in a 1000 cm^3 flask filled up to 250 cm^3 and vibrated for 30 s and the packing density calculations were carried out for each trial. Aggregates having highest packing densities were chosen for further analysis. In the next step, batches were prepared by taking different grades of materials and additives in the proper proportion and are summarized in Tables I and II. The materials were dry mixed in a plastic container for 10 min by spatula and were then used in sample preparation. Generally, ultra and LCCs require less than 5 wt% of water to achieve the desired rheology; therefore, water was added in two steps. The casting was done by adding first two-thirds proportion of water at a time. Then, one-third of water was added slowly to get a homogenous mixing. The wet mixing was performed for up to 5–6 min to achieve proper flow. Immediately after doing wet mixing, the castable mix was filled into a rectangular bar shape mold (152 mm × 25 mm × 25 mm) made of hard steel. The mold was placed on the vibrating table filled with the wet mixed castable and the mixes were vibrated for 10 min, showing better compactness. For each composition, several samples were prepared for laboratory testing. The samples were cured in a moisture-saturated environment (95% RH) in a humidity chamber at room temperature for different time periods. For firing the samples, they were first oven dried at 110°C for 24 h. The test samples were fired at 1300°C–1550°C with a variation of ±5°C in an electric SiC heating element furnace with maximum soaking time of 3 h. The cured samples as well as the fired samples were tested for bulk density, apparent porosity, HMOR, CMOR, and cold crushing strength (CCS). These samples were also analyzed by XRD for phases present and by FE-SEM for their morphological behavior.

(6) Phase Identification

X-ray diffraction patterns were observed using a Rigaku portable XRD machine (Rigaku, Tokyo, Japan). Calcined powdered samples were analyzed by XRD for phases present in the fired sample. Phase identification analysis was carried out by comparing the respective powder XRD patterns with the standard database stated by JCPDF. Detailed analyses of the phase formation and changes over the temperature range and variation in compositions were carried out.

(7) Cold Crushing Strength of HAC and LCC Formulated

The CCS is the capacity of a material to withstand axially directed pushing forces. By definition, the compressive strength of a material is that value of uniaxial compressive strength reached when the material fails completely. CCS of cement was measured as the compressive strength of a 50 mm cement cube made of pure HAC (without any aggregates). These samples were tested for compressive strength after 6, 24, and 48 h, respectively, according to (ASTM C1194-03).

(8) Cold and Hot Modulus of Rupture (CMOR and HMOR) of LCC Formulated

Cold and hot modulus of rupture (CMOR and HMOR) measurements were carried out under three-point bending tests (ASTM C133-97for CMOR and ASTM C583-10for HMOR) using 152 mm × 25 mm × 25 mm samples. CMOR and HMOR were calculated using the following formulae:

$$\mathrm{MOR} = \frac{3PL}{2db^2}$$

where, MOR = modulus of rupture (MPa), P = maximum applied at rupture (N), L = span between supports (mm), b = breadth or width of specimen (mm), and d = depth of specimen (mm). CMOR tests were conducted at room temperature using universal materials test equipment (Model 810, MTS System, Eden Prairie, MN) for samples pre fired at 1300°C, 1350°C, 1400°C, 1450°C, 1500°C, and 1550°C for 3 h. HMOR measurements were made at 1400°C, 1500°C, and 1600°C using Netzsch 414/3 HMOR Equipment (Netzsch, Selb, Germany) for samples pre fired at 1550°C for 3 h, cooled at room temperature and then reheated for testing.

III. Results and Discussion

(1) Evolution of Phases by X-Ray Diffraction

Figures 2 and 3 are the XRD patterns of samples calcined in the range 800°C–1000°C with 70% and 80% alumina to be

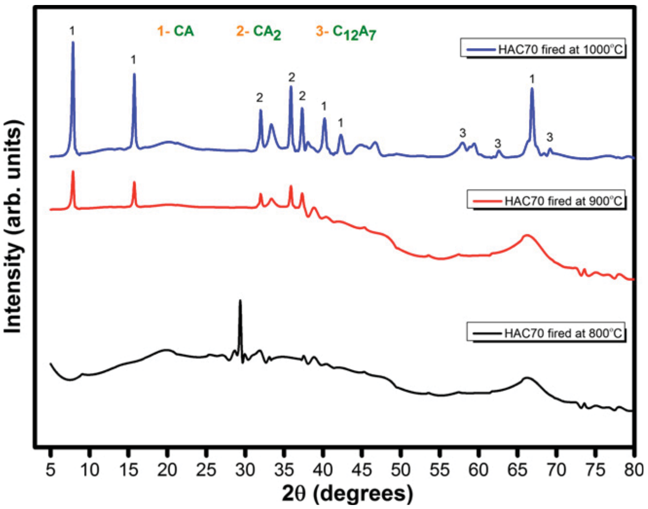


Fig. 2. XRD plot of HAC70.

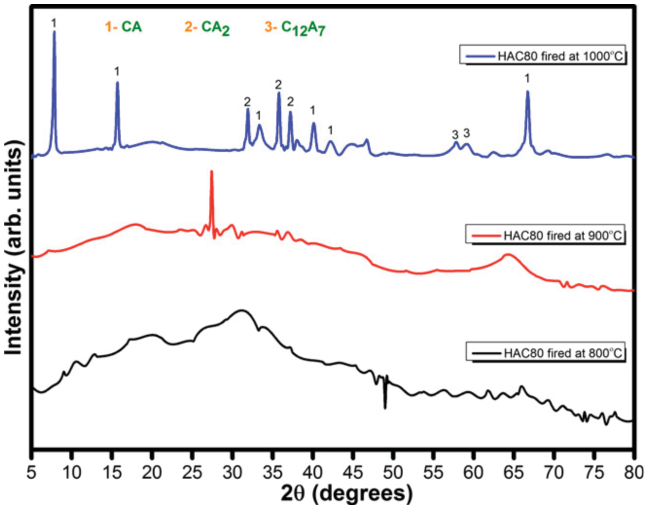


Fig. 3. XRD plot of HAC80.

termed as HAC70 and HAC80, respectively. When calcined below 900°C, these powders proved to have X-ray pseudo-amorphous pattern, where initial formation of calcium-aluminate phases may be envisaged. Pure crystalline cementing phases only begin to form in the temperatures above 900°C in both compositions. A major improvement in crystalline behavior is evident when both cement samples were fired at 1000°C. Prime phases investigated in both compositions included CA, CA$_2$, and C$_{12}$A$_7$, which are readily formed and thermodynamically most stable compounds in the CaO–Al$_2$O$_3$ binary system.[15] These peaks were identified by standard JCPDS cards numbered 41-0358, 34-0440, and 09-0413 for their corresponding peaks of hexagonal CA, monoclinic CA$_2$, and cubic C$_{12}$A$_7$, respectively. In the conventional preparation route by high-temperature solid-state synthesis, the batch usually contains CaO-rich phases and unreacted Al$_2$O$_3$ before the appearance of desired product phase. The formation sequence of phases in these mixtures is always from calcia-rich phases to the alumina rich phase which could be accounted for the formation of C$_{12}$A$_7$ as soaking period was very low 10 min and energy saving.

Presence of broad peaks in XRD patterns of calcined cement powders show that particle size is small. Crystallite size, d of calcined powder was calculated from X-ray line broadening analysis using Scherrer's formula:

$$d = \frac{0.9\lambda}{\beta \mathrm{Cos}\theta}$$

where β is the full width at half maximum intensity of a Bragg reflection excluding instrumental broadening, λ is the wavelength of the X-ray radiation, and θ is the Bragg angle. β is taken for the strongest Bragg's peak corresponding to 2θ. Both samples have crystallite size in the range 20–35 nm.

(2) Setting Behavior of HAC

Figure 4 shows the setting behavior of HAC. The prepared HAC powders were mixed with water (0.85 P). At room temperature, 70% alumina containing cement gave an initial setting time of 16 min and final setting occurred in 45 min. Another composition of HAC having 80% alumina had an initial setting time of 18 min and a final setting time of 60 min. With increasing alumina content in HAC the setting time showed an increasing trend.

(3) CCS of HAC Fired at 1000°C

The pure (without any aggregates) HAC attained good structural strength as obtained from experimental procedure and shown in Fig. 5. Samples were tested after curing for 6, 24, and 48 h, respectively. Sample blocks with inclusion of two commercialized cements of similar compositions with those of as above prepared were made to have a better comparative plot. The strength increased rapidly with curing time in all the compositions. Initially, in 6 h, the CCS value obtained for HAC70 is 10 MPa and for HAC80 is 14 MPa. After 48 h it reached up to 65 and 70 MPa for HAC70 and HAC80, respectively, which is better than the commercially available CA-14M-55 MPa and CA-25C-50 MPa (Almatis). It gets the maximum strength at around 48 h and after this period there is a very slight variation. It can be seen that

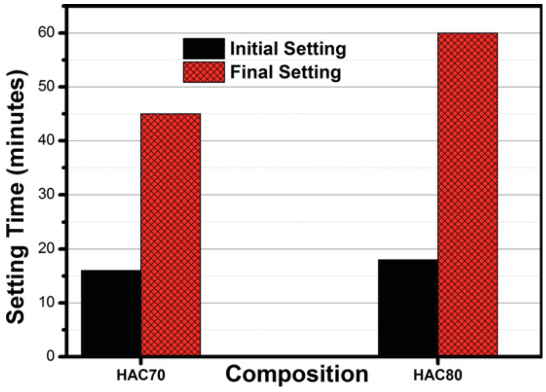


Fig. 4. Setting time behavior of HAC70 and HAC80.

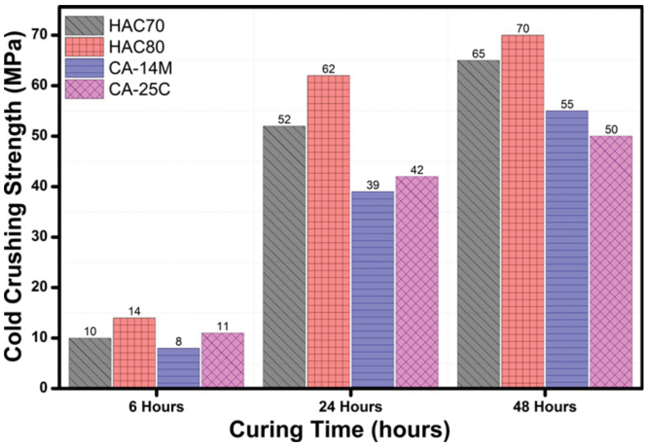
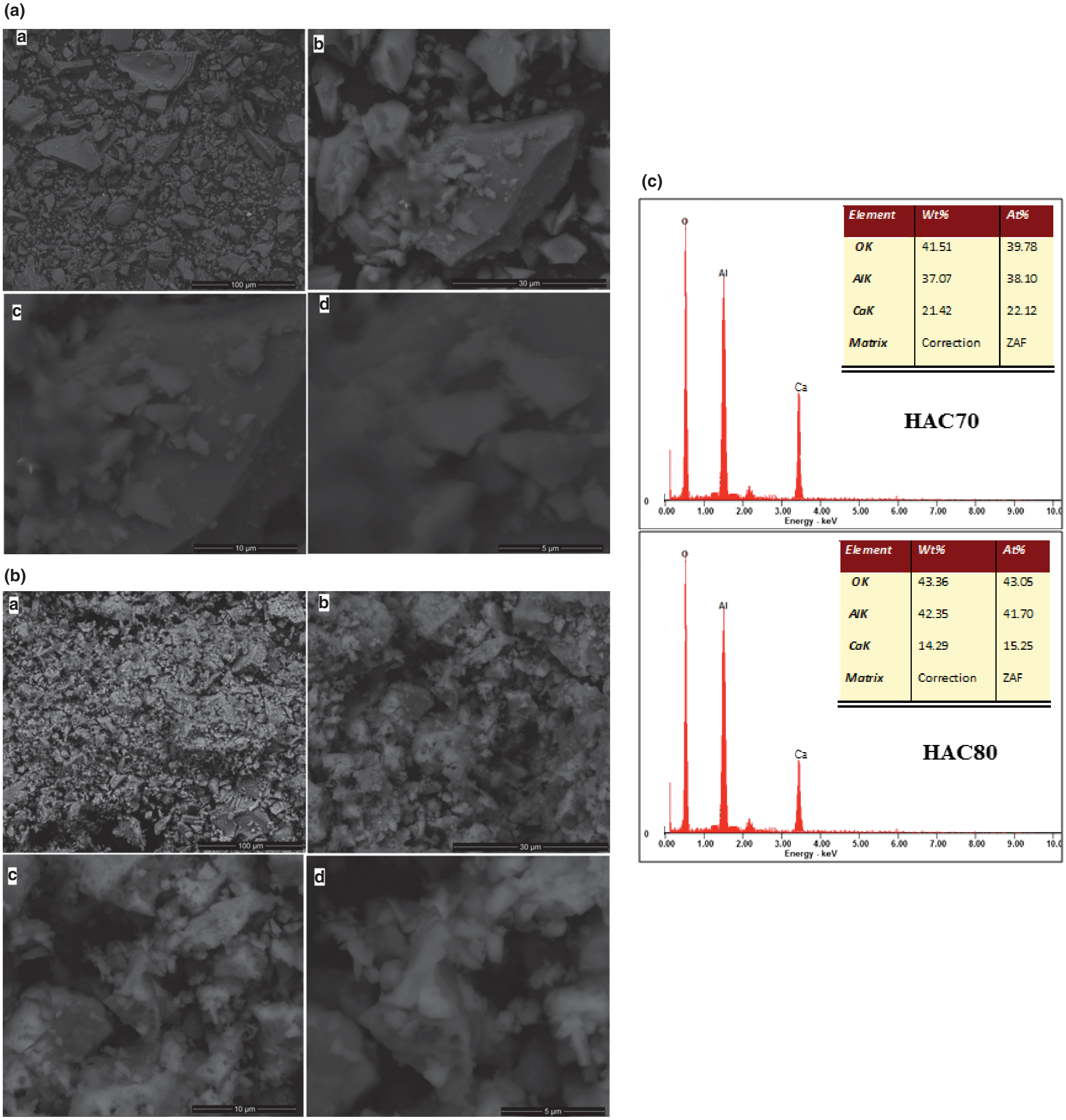


Fig. 5. Cold crushing strength of HAC70 and HAC80.

HAC80 samples have more compressive strength than the HAC70 sample. The higher strength of HAC80 is ascribed to the presence of larger amounts of CA and CA2. It is well-known that CA and $C_{12}A_7$ react significantly in the early ages of hydration, and the hydration of $C_{12}A_7$ is very exothermic, so the formation of stable hydrates generally occurs sooner. Although CA_2 is known to react slowly with water in the early stages of hydration, its presence along with other phases results in an overall faster hydration rate as the heat of hydration resulting from the hydration of CA activates CA_2 and makes it react relatively faster with water than it would do alone, but not more than $C_{12}A_7$. CCS data of the sintered ceramic bodies exhibit high strength of both samples. This is due to the formation of the ceramic bond and absence of any impure phase.[16–19]

(4) FE-SEM of HAC

Figures 6(a) and (b) represents FE-SEM of networks of well-crystallized interlocking hexagonal plates of CA matrix of HAC70 and HAC80 fired at 1000°C, respectively. In both figures a, b, c, d represent different magnifications of same samples. The monoclinic phases of CA_2 and cubic $C_{12}A_7$ can be observed in both figures. High amount of CA and CA_2 is proposed to enhance the refractory properties. $C_{12}A_7$ phase is responsible for high bonding and quick hydration and small cubic crystals of this phase are evident in the most homogeneous distribution of CA phase matrix. Figure 6(c) is the EDS representation of both HAC70 and HAC80, which is a further confirmation of the exact elemental composition and it also a depiction of pure phases obtained.



Element	Wt%	At%
OK	41.51	39.78
AlK	37.07	38.10
CaK	21.42	22.12
Matrix	Correction	ZAF

Element	Wt%	At%
OK	43.36	43.05
AlK	42.35	41.70
CaK	14.29	15.25
Matrix	Correction	ZAF

Fig. 6. (a) FE-SEM of HAC70; (b) FE-SEM of HAC80; (c) EDS pattern of HAC70 and HAC80.

(5) XRD Patterns of Castables Fired at 1550°C for 3 h

Figures 7 and 8 portray XRD patterns of castables fired at 1550°C for 3 h, here R1 to R6 and S1 to S6 indicate castables formulated with HAC70 and HAC80, respectively. The corundum phase appeared as a major component due to the transformation of bauxite minerals to corundum. The second major phase was detected as mullite, which resulted due to the addition of microsilica and reactive alumina in all the castable samples. In both castable series R and S, as we proceed from high to low batch number, the peak intensities of mullite increase this is accounted for increasing micro fine silica content. Although SiC phase was added as a minor ingredients, but it fails to show its intensity peak in all the plots, so it could be extracted from the fact that at high temperatures its oxidation would have occurred forming silica and finally reacting with aluminus content to result in more mullite formation. These peaks were identified by standard JCPDS cards numbered 46-1212, 15-0776 for Fig. 6 and 46-1212, 06-0258 for Fig. 8. Minority peaks of silicon carbide in both figures were identified and matched with JCPDS card number 42-1091.

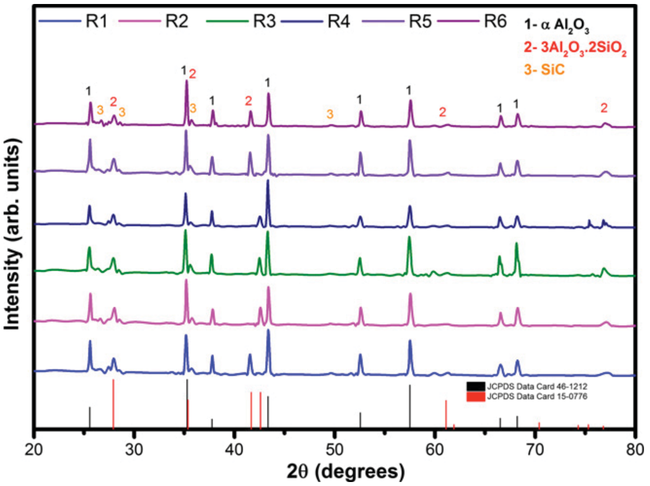


Fig. 7. XRD plot of R series castables prepared with HAC70.

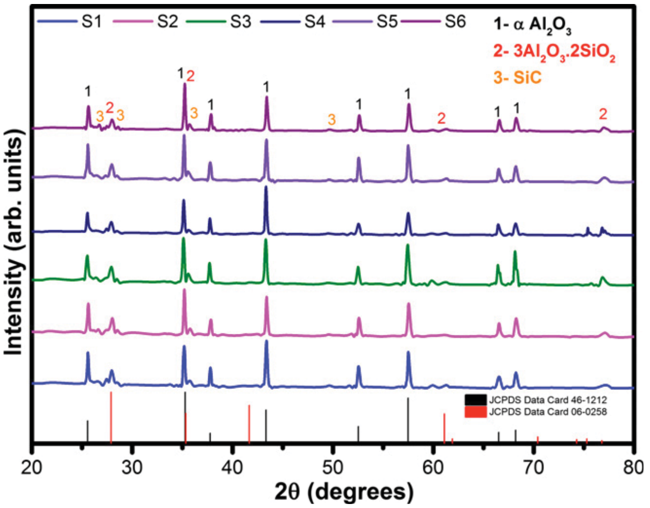


Fig. 8. XRD plot of S series castables prepared with HAC80.

(6) Bulk Density and Apparent Porosity

Table III shows the values corresponding to bulk density, apparent porosity, and thermal shock of R3 and S3 series castables sintered at varying temperature range. Only these series was selected as homologous to their other thermo-mechanical superiority. In the castables prepared, highest bulk densities achieved are 2.91 and 2.93 g/cm^3 for the compositions R3 and S3, respectively. This can be attributed to the use of higher percentages of alumina and micro-fine silica in the aggregate which resulted in most mullite solid solution formations. Apparent Porosity was measured to be in the range of 8%–11% in all the castables prepared.

(7) CCS of Different Castable Compositions Sintered at 1300°C–1550°C for 3 h

Prepared HAC was used for formulating LCC according to the Tables I and II. Reactive Al_2O_3 and microfine SiO_2 content has been varied, which according to the above-mentioned plots resulted in more or less mullite solid solution. This reaction also has a varying effect in the CCS of the castables formulated. In the Figs. 9(a) and (b) depict the castable series S and R, respectively. High values of CCS up to 295–375 MPa was achieved at the maximum sintering temperature 1550°C for S series castables. Similarly, 280–350 MPa was achieved for R series castables. This can be predicted that rise in sintering temperature has a positive effect on the mechanical properties of both series of castables. Formation of mullite strengthens the structure at high temperature and solid solution helps in increasing structural strength. The CCS of the castables prepared with HAC70 and HAC80 were higher in comparison with the CCS of conventional bauxite containing LCC containing Secar71 (160 MPa) and Secar80 (200 MPa).

(8) CMOR and HMOR Different Castable

Cold modulus of rupture strength (CMOR) of castables S and R series is shown in Figs. 10(a) and (b), respectively. It can be seen that CMOR of both series castables has increased with the increasing sintering temperature and was maximum for S3 in which maximum amount of mullite grains was formed. Presence of SiC could also be accounted for high mechanical properties. This was reflected in the strength of the whole castable sample. Hot modulus of rupture (HMOR) of castables R and S series is shown in Figs. 11(a) and (b), respectively. Here, again S3 achieved the maximum strength at high temperature/load. The increase in HMOR values of few samples from 1400°C to 1500°C is due to the formation of mullite solid solutions. To conclude, we may say that the safe range for these types of castables at higher loads is lower than 1600°C. The impurity in the

Table III. Bulk Density, Apparent Porosity, and Thermal Shock Cycles of Prepared Castables

		Temperature (°C)					
Test method	Sample name	1300°C	1350°C	1400°C	1450°C	1500°C	1550°C
Bulk density (gm/cc)	R3	2.60	2.67	2.72	2.80	2.81	2.91
	S3	2.69	2.71	2.76	2.81	2.83	2.93
Apparent porosity (%)	R3	13.00	12.50	11.69	11.41	11.20	11.00
	S3	10.00	9.50	8.90	8.40	8.21	8.00
Thermal shock cycle	R3	16	15	15	14	15	13
	S3	15	16	15	14	14	14

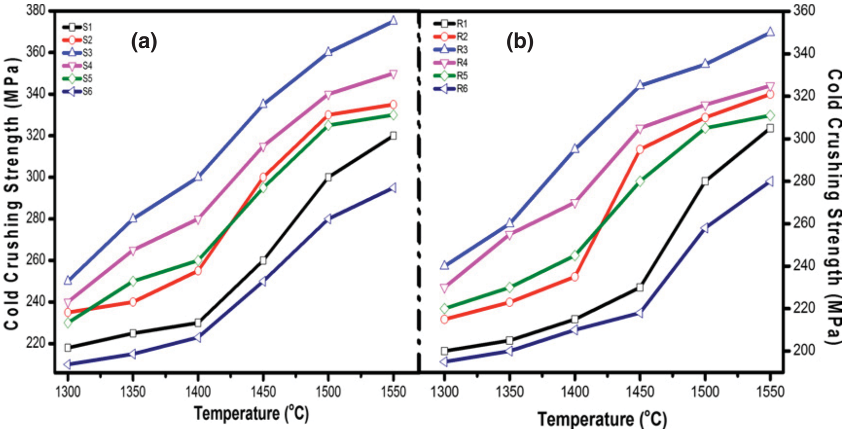


Fig. 9. (a, b) Cold crushing strength of castables.

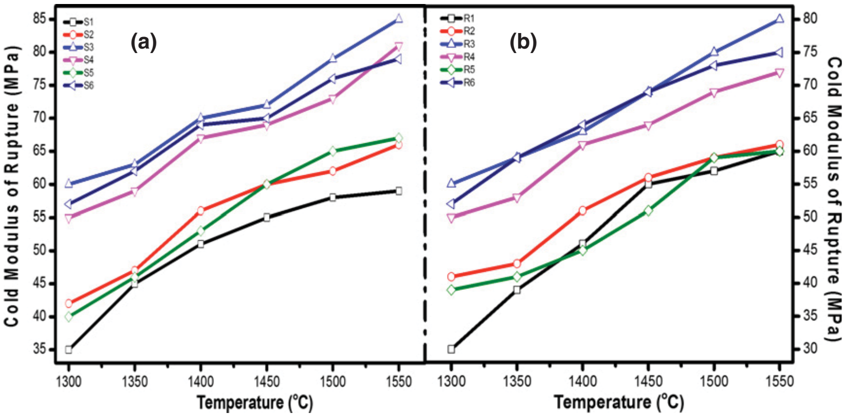


Fig. 10. (a, b) Cold modulus of rupture of castables.

bauxite aggregate increases the liquid phase sintering and mechanical properties, but decreases the porosity.

(9) Thermal-Shock Resistance Tests

Table III displays the thermal shock cycles values evaluated for R3 and S3 series castables. This series was chosen in accordance with their superior thermo-mechanical properties. Thermal-shock resistance tests were run to analyze the influence of the mullite content and the characteristics on the castables thermal-mechanical properties. The tests consisted of 10 heating/cooling cycles (DT = 1200°C). Samples prefired at 1550°C completed one thermal cycle after a holding time of 20 min inside the furnace followed by another 20 min of cooling in air at room temperature. All the S and R series samples exhibited high thermal shock and spalling resistance completing 10 cycles while S3 and R3 attained 16 cycles.

(10) FE-SEM of S3 Castable

The microstructural evolution of castables fired at 1550°C was examined using field-emission scanning electron microscopy of representative regions of fractured specimens. Figure 12(a) depicts FE-SEM photo-micrographs of S3 castable after firing at 1550°C for 3 h where a, b, c, d represent different magnifications. Only S3 series castables were chosen for analysis through FE-SEM as it represented superior thermo-mechanical and physical properties than all other S and R series castables. The matrix includes CA and some of liquid phases. Photo-micrograph exhibits densely packed microstructure with an abundant orthorhombic mullite grain of comparable sizes, embedded in the trigonal corundum matrix. Some needle-shaped mullite beside alumina grains appeared in the microstructure. The presence of such *in situ* formed phase (mullite) had given interlocking nature of

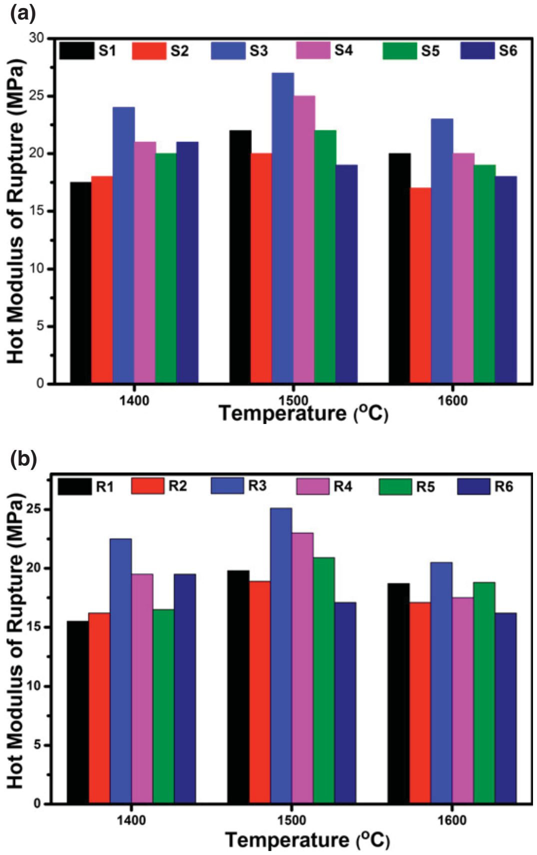
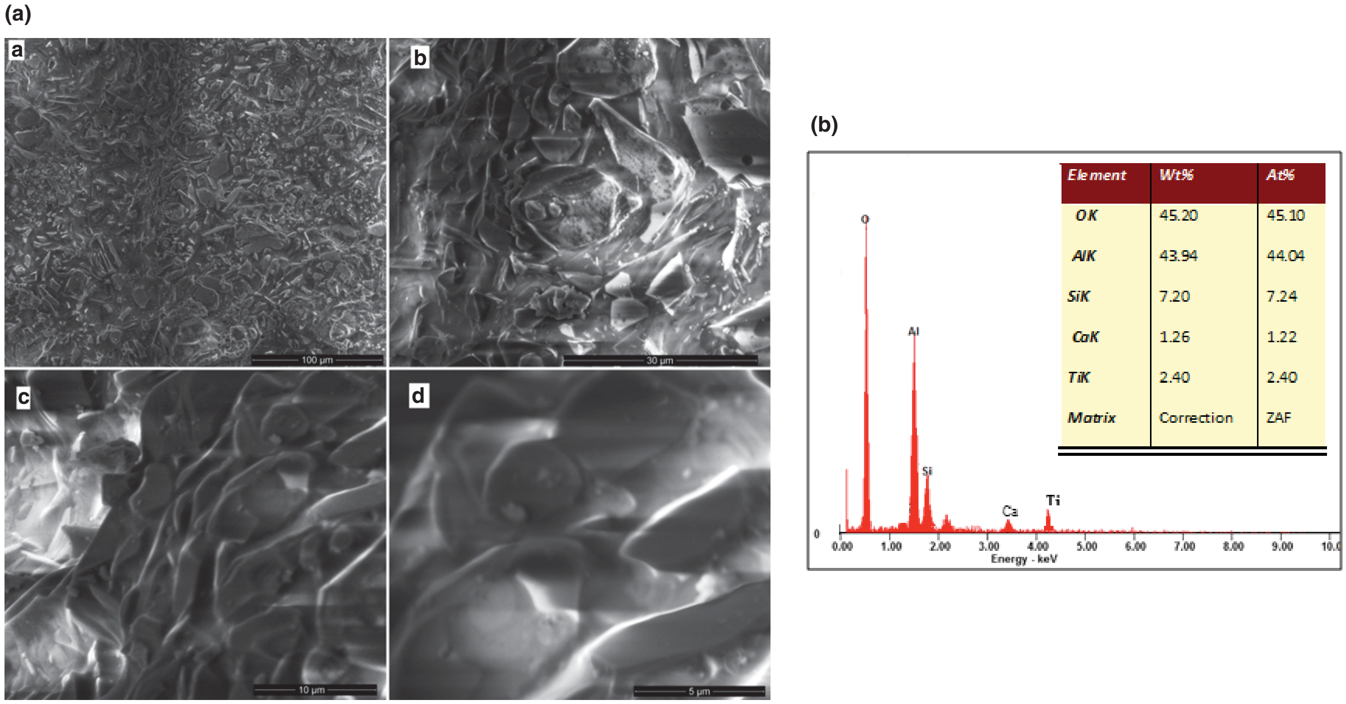


Fig. 11. (a) Hot modulus of rupture of castables prepared with HAC80; (b) hot modulus of rupture of castables prepared with HAC70.



Element	Wt%	At%
OK	45.20	45.10
AlK	43.94	44.04
SiK	7.20	7.24
CaK	1.26	1.22
TiK	2.40	2.40
Matrix	Correction	ZAF

Fig. 12. (a) FE-SEM of S3 castable prepared with HAC80; (b) EDS pattern of S3 castable.

castable and reinforced the matrix confirming the high strength and refractory properties. On the other hand, the impurities that were present in Chinese bauxite may have formed a low melting glassy phases, which tend to decrease the refractory properties and their microstructure may appear as partially diffused structure in some regions. This property is more evident when we zoom into the microstructures while moving a to d in each plot. The EDS pattern of S3 castable is portrayed in Fig. 12(b), which is in correspondence with exact stoichiometric composition of the formulated block. The influence of trace impurities presented during the processing of ceramics is well-known and exploited in the control of densification, grain growth, and morphology during sintering.[20] The ability to control microstructure is important for achieving desired properties.

IV. Conclusion

Novel process synthesized HACs were successfully prepared with very small crystallite size ranging 20–35 nm. Cementing behavior promises a new era of industrial evolution through commercial implementation. Desired cementing phases having high refractoriness similar to CA, CA_2, $C_{12}A_7$ were formed at a very low temperature. One advantage of this process is to exclude silicate phases having low eutectic temperatures in such cements. These silicate phases decrease the refractoriness and the cement cannot be used at higher temperatures. The XRD patterns of castables containing Bauxite and SiC show new phases formed such as corundum and mullite, which were responsible for superior thermo-mechanical and physical properties. Castable samples prepared by HAC having 80% alumina have better physical and cementing properties than the HAC having 70% alumina. Needle like mullite formed at high temperature acts as a bonding phase which was responsible to increase the CMOR. FE-SEM represents dense microstructure of all the samples and glassy phase appearance is due to the impurities present in bauxite.

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Auto-combustion processed high alumina cement and its implementation as bauxite based low cement castables

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Abstract

The present work involved solution combustion synthesis of high alumina cements from their metal nitrate precursors, using urea as an organic fuel. Combusted aluminium nitrate, calcium nitrate and urea complexes leads to formation of high alumina cement at temperature as low as 800 °C. The prime cementing phases observed were CA, CA_2 and $C_{12}A_7$. The second stage of work evaluates, the role of this high alumina cement (HAC) on bauxite based low cement castables. The effect of micro-fine Cr_2O_3 and MgO additions on the sinterability and thermo-mechanical strength of these castables was also investigated. Phase identification and microstructural evaluation of the sintered castables confirms spinel and corundum phase formation. Addition of nano structured cements in refractory castables improved the thermo-mechanical properties to a significant extent.

Keywords: A. Powders: chemical preparation; A. Sintering; C. Mechanical properties; D. Al_2O_3; E. Refractories

1. Introduction

Iron and steel making industries being the chief consumer of refractories have made major improvements in the quality and consistency of their products [1]. Demand for structural and clean steel in this century has increased manifold which in turn prompted for better refractories [2–4]. A significant advancement in refractory technology is hence, continually required to meet the service conditions. Evolution of monolithic for a refractory construction in the present day scenario shows a remarkable increase, due mainly to certain advantages they offer, especially in comparison with shaped articles [5–7]. The properties of these castables have been exceedingly better than bricks with comparable chemistries. With the changes in technology it is now necessary to overcome the limitation of conventional castables (15–20% of calcium aluminate cements), due to its low hot strength, especially when molten slag and metal are present [9]. The most noticeable improvement in monolithic refractory is low cement/low moisture castable development [8]. In the new monolithic refractories technology, low and ultra-low cement castables have an ever-decreasing amount of high alumina cement and its corresponding water for placement. Low cement and low water improves high temperature properties. As CaO forms eutectic by slag dissolution, therefore, it became obvious to reduce the CaO content of the castables which meant reducing the cement and water content. To meet the required service condition, this is how the concept of low cement castables developed [10]. There has been a rapid development in the use of low cement castables in many industries such as non-ferrous metals, cements, petrochemicals and of course in iron and steel industry [11]. These give excellent results in reheating furnaces, ladle linings, soaking pit bottoms, blast furnace troughs. The superior properties of the low cement castables helped the iron and steel makers to reduce their consumption enormously and hence their operating cost.

Solid state synthesis of calcium aluminates require high temperatures and full conversion is not guaranteed. Moreover, it is difficult to obtain a compositionally homogeneous product with this method. In recent years, combustion synthesis has attracted a great deal of attention to produce superfine, un-agglomerated, multicomponent crystalline ceramic without intermediate decomposition or calcination [12]. This method

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exploits an exothermic, rapid and self-sustaining chemical reaction. Its key feature is that the reaction itself provides the heat required to drive the chemical reaction without any external source [13–15].

Commercial high alumina cements are known to contain various phase viz., CA, CA_2, $C_{12}A_7$ and α-alumina whose hydration behavior is interdependent and not yet fully understood [16–19]. The mono calcium aluminate (CA) imparts high mechanical strength and refractoriness to the cement, where rapid setting is mostly associated with $C_{12}A_7$ which dissolves rapidly [20–22]. Cement with high amount of CaO has many drawbacks when used as hydraulic binders in refractory castables. Their excess water demand during casting process, porosity due to drying and also in their low refractoriness when in contact with SiO_2.

There has been enormous amount of work in the field of solution derived combustion of calcium aluminates, however there is lack of studies which focus on their utilization as castables. Present work opens new doors by implementation of prepared cement as monoliths and their hot properties. In the first part, the work that follows describes the synthesis of high alumina cements (CA, CA_2 and $C_{12}A_7$) by the auto combustion reaction of redox mixtures of the corresponding water-soluble nitrate salts with urea. For reference study, a comparison with commercial high alumina cement is reported herein. In the second stage of work, formulation as well as characterization of bauxite castables and prepared cement as the binder is discussed to assess and achieve a good quality of low cement castable. Together, the aluminates and the micro fillers are responsible for the hydraulic setting of the castable. With packing density maximized, the low cement castables are characterized by their low porosity, high density and exceptional hot strength; with enhanced erosion, corrosion, and spalling resistance [23–25].

2. Experimental procedure

2.1. Materials

The starting raw materials A.R. grade aluminum nitrate $Al(NO_3)_3 \cdot 9H_2O$, calcium nitrate $Ca(NO_3)_2 \cdot 4H_2O$, urea $(NH_2)_2CO$, chromium oxide (Cr_2O_3) magnesium oxide (MgO) powder and Chinese bauxite were supplied by Loba Chemie Pvt. Ltd., Mumbai India. The calcined Chinese bauxite that was used in castable formulation in the present study contained approximately 88.60%, 4.78%, 1.58%, 4.0%,0.26%,0.08% and 0.70% by weight Al_2O_3, SiO_2, Fe_2O_3, TiO_2, CaO, Na_2O and others, respectively, as specified by the supplier (Shiva Minerals, Rourkela, India).

2.2. HAC powder preparation

Combustion synthesis or self-propagating high temperature synthesis is a versatile method used for the synthesis of a variety of solids. The method makes use of a highly exothermic reaction between the reactants to produce a flame due to spontaneous combustion which then yields the desired product or its precursor in finely divided form. In order for combustion to occur, initial mixture of reactants should be highly dispersed and has must have high chemical energy. Even if the desired product is not formed immediately after combustion, the fine particulate nature of the product facilitates its formation on further heating. Reaction times are very short since the desired product results soon after the combustion.

The auto-combustion synthesis technique consists of bringing a saturated aqueous solution of the desired metal salts and a suitable organic fuel to boil, until the mixture ignites and a self-sustaining and rather fast combustion reaction takes off, resulting in a dry, usually crystalline oxide powder. While redox reactions such as this are exothermic and often lead to explosion if not controlled, the combustion of metal nitrates and urea mixtures usually occurs as a self-propagating and non-explosive exothermic reaction. The large amounts of gases formed can result in visible flame, which can reach temperatures in excess of 1000 °C.

Aluminum nitrate $Al(NO_3)_3 \cdot 9H_2O$ and calcium nitrate $Ca(NO_3)_2 \cdot 4H_2O$ were weighed and mixed on a laboratory scale to wt ratio of 7:3 and 8:2 of Al_2O_3/CaO, which were denoted as HAC70 and HAC80 high alumina cements, respectively. For complete dissolution of the salts, the solution was kept on a hot plate at around 60 °C with simultaneous stirring until a clear transparent solution was obtained. To this precursor solution urea was poured keeping a cement precursor/fuel ratio of 1:1. The prepared gel was air-dried in an oven at 80 °C to complete dryness. Finally, after the solution was converted to a dried gel powder it was calcined, for 15 min, in air at 500 °C, and then quenched to room temperature. During the first few minutes of the calcinations process, ignition took place with a rapid evolution of large amounts of gases. Therefore, only small portions of the gels were calcined. The synthesis technique use the heat energy released by the redox exothermic reaction at a relatively low ignition temperature between metal nitrates and urea. The process lasted for a relatively short time, so that the particles could be maintained to the nanometer scale. Further high alumina cements nano composite powders were heated at 800 and 1000 °C in a platinum dish using a SiC muffle furnace for a soaking period of 2 h. After heating the HAC powder was stored in desiccator. The probable chemical reactions are given below:

$$2Al(NO_3)_3 \cdot 9H_2O + Ca(NO_3)_2 \cdot 4H_2O + xCO(NH_2)_2 \overset{\Delta}{\Longrightarrow} CaO \cdot Al_2O_3 + xCO_2 + (22+2x)H_2O + (4+x)N_2 \quad (1)$$

$$4Al(NO_3)_3 \cdot 9H_2O + Ca(NO_3)_2 \cdot 4H_2O + xCO(NH_2)_2 \overset{\Delta}{\Longrightarrow} CaO \cdot 2Al_2O_3 + xCO_2 + (40+2x)H_2O + (7+x)N_2 \quad (2)$$

$$14Al(NO_3)_3 \cdot 9H_2O + 12Ca(NO_3)_2 \cdot 4H_2O + xCO(NH_2)_2 \overset{\Delta}{\Longrightarrow} 12CaO \cdot 7Al_2O_3 + xCO_2 + (174+2x)H_2O + (33+x)N_2 \quad (3)$$

2.3. HAC powder characterization

X-ray diffraction patterns were determined using a Rigaku portable XRD machine (Rigaku, Tokyo, Japan). Calcined powders were analyzed by XRD to identify the cementing phases present. Phase identification analysis was carried out by comparing the respective powder XRD patterns with the standard database stated by JCPDF. Detailed studies of the phase formation and changes over the temperature range and variation in compositions were carried out.

HAC powders calcined at 1000 °C were analyzed for their microstructure at different magnifications with the help of FEI Quanta 200 F field emission scanning electron microscope.

2.4. Castable formulation and characterizations

Low cement refractory castables are generally prepared using approximately 3 to 5 wt% HAC and refractory grade bauxite with certain additives. In the first step for cement castable formulation, calcined bauxite was oven dried, crushed, and ground for grading into different sizes in a planetary ball mill. The jar and grinding media were of titanium-coated stainless steel material. At one time 300 g of calcined bauxite material was taken in a jar and ground in a high energy planetary ball mill for 15 min at 600 rpm. Similarly, it was processed to complete the grinding of complete material. The ground material was then kept in various selected sieves and set up on the motorized vibro-sieving equipment for grading. After separation of different graded bauxite, experiments were performed further. The nature of ultra-fine particles decide the high temperature properties like creep behavior, corrosion resistance and hot strength. The trials of aggregate proportions were taken in a 1000 cm^3 flask filled up to 250 cm^3 and vibrated for 30 s and the packing density calculations were carried out for each trial. Aggregates having higher packing densities were chosen for further analysis. In the next step, batches were prepared by taking different grades of materials and additives in the proper proportion and are summarized in Tables 1 and 2. The materials were dry mixed in a plastic container for 10 min with a spatula and then were taken for sample preparation. Generally, ultra and LCCs require less than 5 wt% of water to achieve the desired rheology; therefore, water was added in two steps. The casting was done by adding the first two-thirds proportion of water at a time. Then, one-third of water was added slowly to get a homogeneous mixing. The wet mixing, was performed for up to 5–6 min to achieve proper flow. Immediately after wet mixing, the castable mix was filled into a rectangular bar shape mould (152 mm × 25 mm × 25 mm) made of hard steel. The mould was placed on the vibrating table filled with the wet mixed castable and the mixes were vibrated for 10 min, resulting in better compactness. For each composition, several samples were prepared for laboratory test. The samples were cured in a moisture-saturated environment (95% RH) in a humidity chamber at room temperature for different time periods. For firing the samples, they were first oven dried at 110 °C for 24 h. The test samples were fired at 1300–1550 ± 5 °C in an electric furnace, with SiC heating element and a soaking time of 3 h. The cured samples as well as the fired samples were tested for their bulk density, apparent porosity (ASTM C20-00), HMOR (ASTM C583-10), CMOR (ASTM C133-97) and cold crushing strength (ASTM C1194-03). These samples were also analyzed by XRD for phases present and by SEM for their morphological behavior.

Table 1
Batch composition with HAC70.

Sample	HAC70 (wt%)	Chinese bauxite (wt%)	Microfine MgO (wt%)	Microfine Cr_2O_3 (wt%)
P1	5	85	9	1
P2	5	85	8	2
P3	5	85	7	3
P4	5	85	6	4
P5	5	85	5	5
P6	5	85	4	6
P7	5	85	3	7
P8	5	85	2	8

Table 2
Batch composition with HAC80.

Sample	HAC80 (wt%)	Chinese bauxite (wt%)	Microfine MgO (wt%)	Microfine Cr_2O_3 (wt%)
Q1	5	85	9	1
Q2	5	85	8	2
Q3	5	85	7	3
Q4	5	85	6	4
Q5	5	85	5	5
Q6	5	85	4	6
Q7	5	85	3	7
Q8	5	85	2	8

3. Results and discussion

3.1. Evolution of phases by X-ray diffraction

Figs. 1 and 2 are the XRD patterns of samples calcined at 800 °C and 1000 °C with 70 and 80% alumina termed as HAC70 and HAC80, respectively. The effect of calcining steps for 2 h at 800 and 1000 °C was investigated. For all the aluminates, calcining steps at high temperatures only promote the degree of crystallinity and grain growth. The mixtures ignited as soon as they were placed inside the furnace pre-heated at 500 °C. The reactions were rapid and produced greyish white and lacy dry foams, accompanied by a great volume increase. But the temperature was not enough to promote the crystallization of the desired phase. When calcined below 800 °C, these powders proved to have X-ray pseudo-amorphous pattern, where the initial formation of calcium–aluminate phases may be envisaged. When the calcining temperature was brought up to 1000 °C signs of the crystalline aluminate is detected in the X-ray diffraction pattern. In spite of the short reaction time, X-ray diffraction of the as-prepared powders showed, respectively, well crystallized CA, CA_2, and $C_{12}A_7$ (full conversion) as the only phases present at 1000 °C. Prime phases investigated in both are

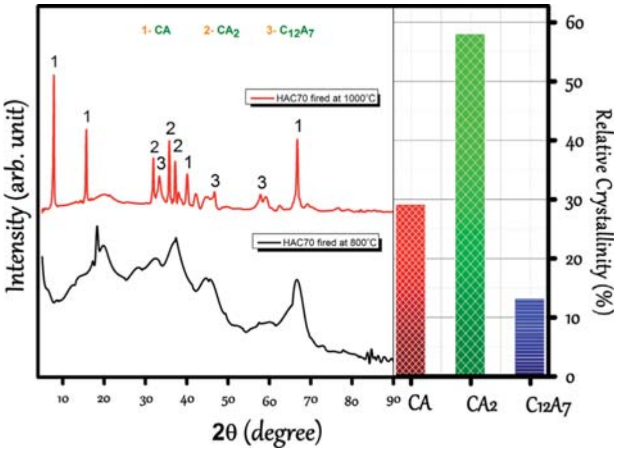

Fig. 1. XRD plot of HAC70.

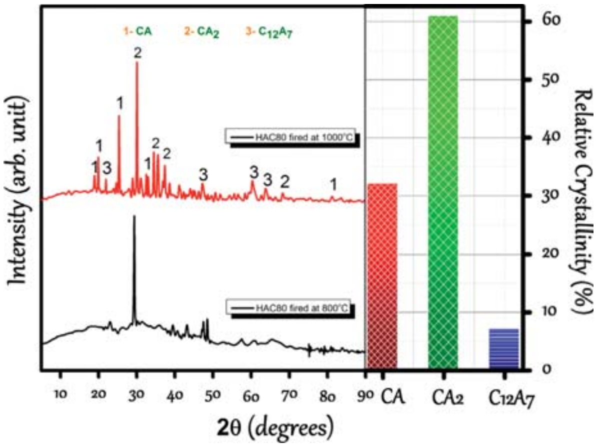

Fig. 2. XRD plot of HAC80.

readily formed and thermodynamically most stable compounds in the CaO–Al_2O_3 binary system. These peaks were identified by standard JCPDS cards numbered 41-0359, 34-0442, and 09-0412 for their corresponding peaks of hexagonal CA, monoclinic CA_2 and cubic $C_{12}A_7$, respectively. In the conventional preparation route by high-temperature solid-state synthesis, the batch usually has CaO-rich phases and unreacted Al_2O_3 before the desired product phase appears. The formation sequence of phases in these mixtures is always from calcia-rich phase to the alumina rich phase which could be accounted for $C_{12}A_7$ formation, as soaking period was very low. Presence of broad peaks in XRD patterns of calcined cement powders show that particle size is small. Crystallite size, d of calcined powder was calculated from X-ray line broadening analysis using Scherer's formula:

$$d = \frac{0.9\lambda}{\beta \text{ Cos } \theta} \tag{4}$$

where β is the full width at half maximum (FWHM) intensity of a Bragg reflection excluding instrumental broadening, λ is the wavelength of the X-ray radiation and θ is the Bragg angle. β is taken forth strongest Bragg's peak corresponding to 2θ. Both samples have crystallite size in the range 18–38 nm.

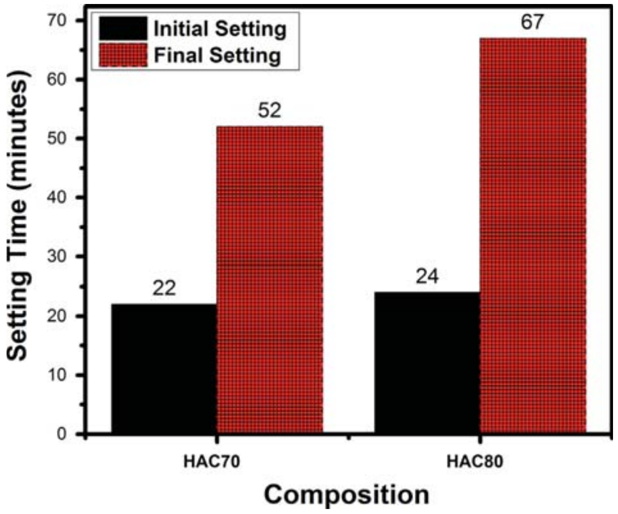

Fig. 3. Setting time behavior of HAC70 and HAC80.

3.2. Setting behavior of HAC

Fig. 3 shows the setting behavior of HAC. The prepared HAC powders were mixed with water (0.85 P). The initial major hydration products of calcium aluminate cement are CAH_{10} and C_2AH_8. With the passage of time these products are replaced by C_3AH_6 and AH_3 at rates that depend on the temperature and other factors; this process is called conversion. An amorphous or gel phase containing Ca^{2+} forms simultaneously with the crystalline products. In the subsequent course of the reaction, essentially an induction period occurs during which the concentrations remain near their maximum values, the rates of dissolution and precipitation thus being approximately equal. The precipitation products nucleate and grow; these processes begin slowly, but accelerate. Ultimately, precipitation is massive, the concentrations drop and in a paste, setting occurs. In the conversion reaction, CAH_{10} and C_2AH_8 redissolve and C_3AH_6 is formed, together with additional AH_3, the structure of which then approximates to that of gibbsite. At room temperature, 70% alumina containing cement gave an initial setting time of 22 min and final setting occurred in 52 min. Another composition of HAC having 80% alumina had an initial setting time of 24 min and a final setting time of 67 min. With increasing alumina content in HAC the setting time showed an increasing trend.

3.3. CCS of HAC fired at 1000 °C

The pure (without any aggregates) HAC attained good structural strength as obtained from experimental procedure and shown in Fig. 4. Samples were tested after curing for 6, 24 and 48 h. Sample blocks with the inclusion of two commercialized cements of similar compositions with those of as above prepared were made to have a comparative study. The strength increased rapidly with curing time in all the compositions. In high alumina containing cement system, saturation of $Al(OH)^{4-}$ ions lead to an increase of the pH and the ionic strength of the aqueous medium. This reduces the hydration rate at early ages and high early strength is not achieved, until nuclei of calcium aluminate hydrates are formed. Eventually the formation of denser stable hydrates (C_3AH_6 and AH_3) occur. So, initially, in 6 h, the CCS value obtained for HAC70 is 10 MPa and for HAC80 is 12 MPa. After 48 h it reached up to 65 and 72 MPa for HAC70 and HAC80, respectively, which is better than the commercially available CA-14M-55 MPa and CA-25C-50 MPa (Almatis). It gets the maximum strength at around 48 h and after this period there is a very slight variation. It can be seen that HAC80 samples has more compressive strength than the HAC70 sample. The higher strength of HAC80 is ascribed to the presence of larger amounts of CA and CA_2. It is well-known that CA and $C_{12}A_7$ react significantly in the early ages of hydration, and the hydration of $C_{12}A_7$ is very exothermic, so the formation of stable hydrates generally occurs sooner. Although CA_2 is known to react slowly with water in the early stages of hydration, its presence along with other phases results in an overall faster hydration rate as the heat of hydration resulting from the hydration of CA activates CA_2 and makes it react relatively faster with water than it would do alone, although lesser than $C_{12}A_7$. CCS data of the sintered ceramic bodies exhibit high strength of both samples. This is due to the formation of the ceramic bond and the absence of any impure phase.

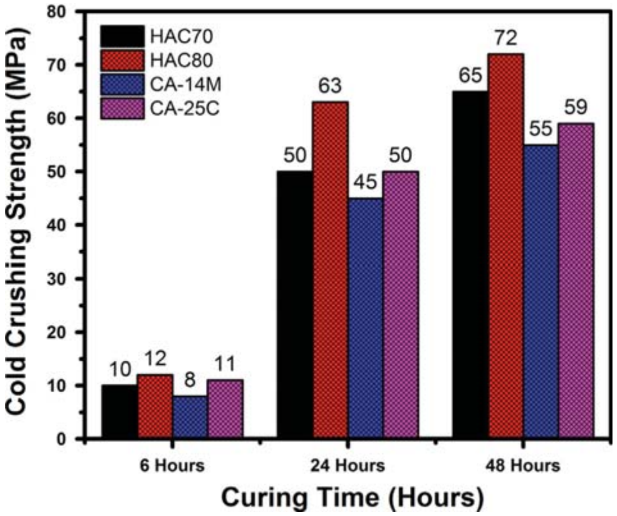

Fig. 4. Cold crushing strength of HAC70 and HAC80.

3.4. SEM of HAC

Fig. 5(A) and (B) represent the SEM of networks of well-crystallized interlocking hexagonal plates of CA matrix of HAC70 and HAC80 fired at 1000 °C, respectively. In both figures a, b, c, d represents different magnifications of same sample. The monoclinic phases of CA_2 and cubic $C_{12}A_7$ can be observed in both figures. CA produced the finest particles, with euhedral crystals loosely agglomerated. CA_2 crystals are similar in shape but larger, and the agglomerates show signs of incipient sintering. $C_{12}A_7$ crystals, on the contrary, in spite of crystallizing in the cubic system, are needle-like and enveloped by a transparent sheath, suggesting that nuclei grow from a glassy material. The higher amount of CA and CA_2 is proposed to enhance the refractory properties. $C_{12}A_7$ phase is responsible for high bonding and quick hydration and small cubic crystals of this phase are evident in the most homogeneous distribution of the CA phase matrix.

3.5. XRD patterns of castables fired at 1550 °C for 3 h

Figs. 6 and 7 portray XRD patterns of castables fired at1550 °C for 3 h, here P1 to P8 and Q1 to Q8 indicate castables formulated with HAC70 and HAC80, respectively. The corundum phase appeared as a major component due to the transformation of bauxite minerals to corundum. The second major phase was detected as spinel ($MgAl_2O_4$).

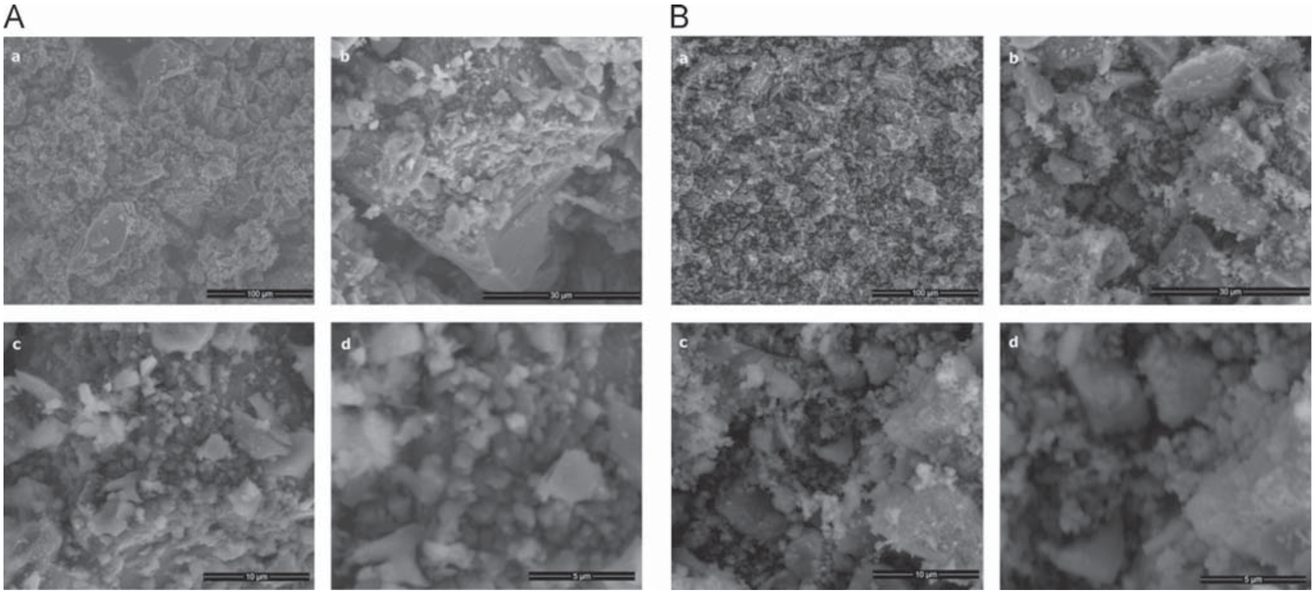

Fig. 5. (A) SEM of HAC70. (B) SEM of HAC80.

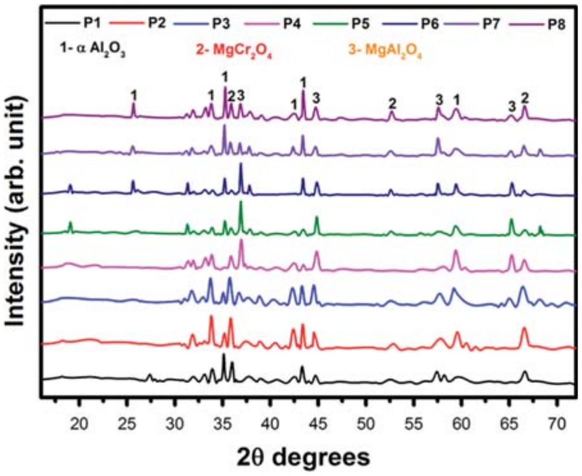

Fig. 6. XRD plot of P series castables prepared with HAC70.

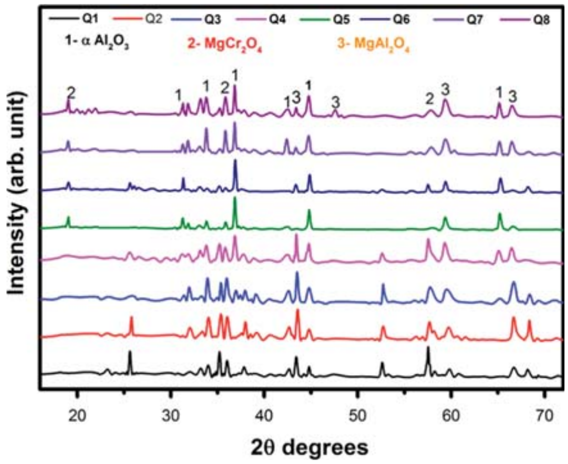

Fig. 7. XRD plot of Q series castables prepared with HAC80.

Table 3
Bulk density, apparent porosity and thermal shock cycles of prepared castables.

Test method	Temperature (°C)						
	Sample name	1300	1350	1400	1450	1500	1550
Bulk density (gm/cm^3)	P2	2.75	2.90	3.00	3.05	3.20	3.21
	Q2	2.80	2.95	3.10	3.15	3.29	3.32
Apparent porosity (%)	P2	10.69	10.61	9.91	9.80	9.20	9.00
	Q2	8.90	8.80	8.60	8.50	8.15	8.00
Thermal shock cycle	P2	15	14	14	15	15	16
	Q2	14	16	14	15	16	18

Appearance of $MgCr_2O_4$ spinel also occurred as a minor peak which resulted due to the interaction of MgO and Cr_2O_3 in all the castable samples. In both castable series P and Q, as we proceed from high to low batch number, the peak intensities of spinel increase this is accounted for increasing micro fine MgO and Cr_2O_3 content. These peaks were identified by standard JCPDS cards numbered 81-2267, 82-1529, 77-438, and 89-4203 for Fig. 6 and 89-7716, 82-1529, 86-0095, 89-4921 for Fig. 7.

3.6. Bulk density, apparent porosity and thermal shock cycles of prepared castables

Table 3 shows the values corresponding to bulk density, apparent porosity, and thermal shock of P2 and Q2 series castables sintered at varying temperature range. Only these series was selected as homologous to their other thermo-mechanical superiority. In the castables prepared, highest bulk densities achieved are 3.21 and 3.32 g/cm^3 for the compositions P2 and Q2, respectively. This can be attributed to the use of higher percentages of alumina and micro-fine MgO which lead to in-situ spinel formation. The densification can also be attributed to Al_2O_3–Cr_2O_3 system which forms substitutional solid solution $(Al_{2-x}Cr_x)_2O_3$ $(0 \leq x \leq 2)$ over an entire range of composition at high temperature without formation of any eutectic, as they have the same corundum crystal structure consisting of a hexagonal close packed array of oxygen anions with two-third of the octahedral interstitials occupied by the cations [26]. Apparent porosity was measured to be in the range of 8–10.69% in all the castables prepared. Table 3 displays the thermal shock cycle values evaluated for Q2 and P2 series castables. This series was chosen in accordance with their superior thermo-mechanical properties. Thermal-shock resistance tests were run to analyze the influence of the corundum and spinel content and the characteristics on the thermal-mechanical properties of castables. The tests consisted of 10 heating/cooling cycles (DT = 1200 °C). The thermal shock is the generation of thermo-mechanical stresses in the material from the sudden change in temperature. When the tensions generated are greater than the breakdown strain of the material, nucleation and crack propagation occurs, damaging the structure of the material. Samples prefired at 1550 °C completed one thermal cycle after a holding time of 20 min inside the furnace followed by another 20 min of cooling in air at room temperature. All the Q and P series samples exhibited high thermal shock and spalling resistance completing 12 cycles while Q2 and P2 attained 18 and 16 cycles, respectively. Such high spalling resistance is attributed to irregular in-situ spinelisation which inhibits the crack development and growth due to abrupt temperature changes.

3.7. CCS of different castable compositions sintered at 1300 °C–1550 °C for 3 h

Prepared HAC was used for formulating LCC according to Tables 1 and 2. Micro fine MgO and Cr_2O_3 content has been varied, which according to the above mentioned plots resulted in corundum and spinel phase formation. This reaction also has a varying effect in the CCS of the castables formulated. In Fig. 8(a) and (b) depict the castable series Q and P, respectively. High values of CCS up to 151–285 MPa was achieved at the maximum sintering temperature 1550 °C for Q series castables. Similarly, 145–279 MPa was achieved for P series castables. It may be predicted that the rise in sintering

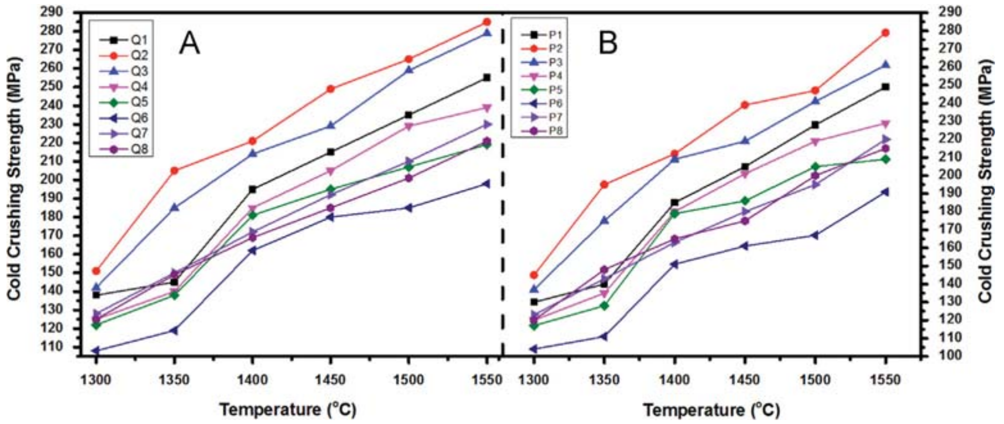

Fig. 8. ((a) and (b)) Cold crushing strength of castables.

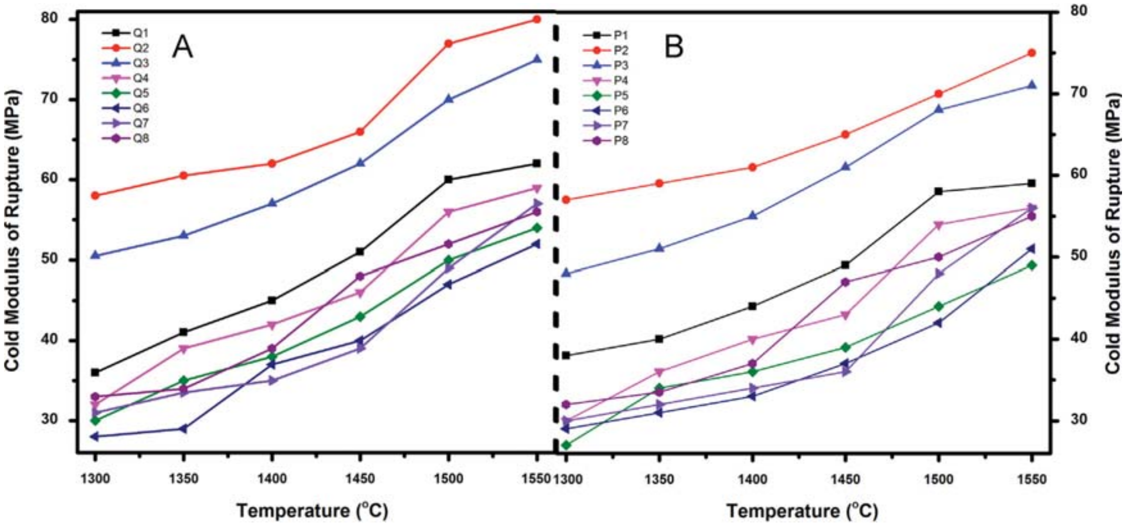

Fig. 9. ((a) and (b)) Cold modulus of rupture of castables.

temperature gives grain to grain interlocking, reducing intergranular porosity. This has a positive effect on the mechanical properties of both series of castables. Formation of spinel strengthens the structure at high temperature and mullite solid solution helps in increasing densification. The CCS of the castables prepared with HAC70 and HAC80 were higher in comparison with the CCS of conventional bauxite containing LCC containing Secar-71(140 MPa) and Secar80 (200 MPa).

3.8. *CMOR and HMOR different castable*

Cold modulus of rupture strength (CMOR) of castables Q and P series is shown in Fig. 9(a) and (b), respectively. It can be seen that CMOR of both series castables has increased with the increasing sintering temperature and was maximum for Q2 in which maximum amount of corundum and spinel grains was formed. MgO–Cr_2O_3 spinelisation could also be accounted for high mechanical properties as this reaction has an expansive nature, hence the microcracks generation plays a positive role in strength development. This was reflected in the strength of the whole castable sample. Hot modulus of rupture (HMOR) of castables Q and P series is shown in Fig. 10(a) and (b), respectively. Here, again Q2 achieved the maximum strength at high temperature/load. The increase in HMOR values of few samples from 1400 to 1600 °C is due to the formed magnesium aluminate spinel and alumina-chrome solid solutions. CaO in the cement is favorable for the presence of a liquid phase at high temperatures, which helps to accommodate thermo-mechanical stresses generated and thereby, improving hot properties. High-temperature tensile ductility in fine-grained Al_2O_3 is an extensively researched phenomena which is enriched by small amounts of secondary phases. For enhancement of this phenomenon, suppression of alumina grain growth and co-dispersion of spinel, magnesia or zirconia particle is required. The reaction derived in-situ spinel as observed through XRD patterns, here acts as dispersive agent in corundum. Due to this superplastic behavior, rise in the high temperature bending strengths is observed when magnesia is added incrementally. Abnormal grain growth of bauxite is suppressed as is seen by microstructural plots even though

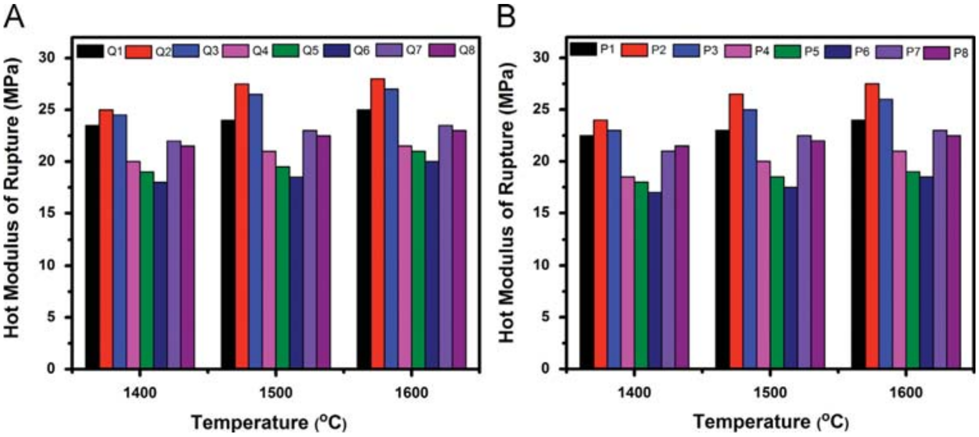

Fig. 10. (a) Hot modulus of rupture of castables prepared with HAC80. (b) Hot modulus of rupture of castables prepared with HAC70.

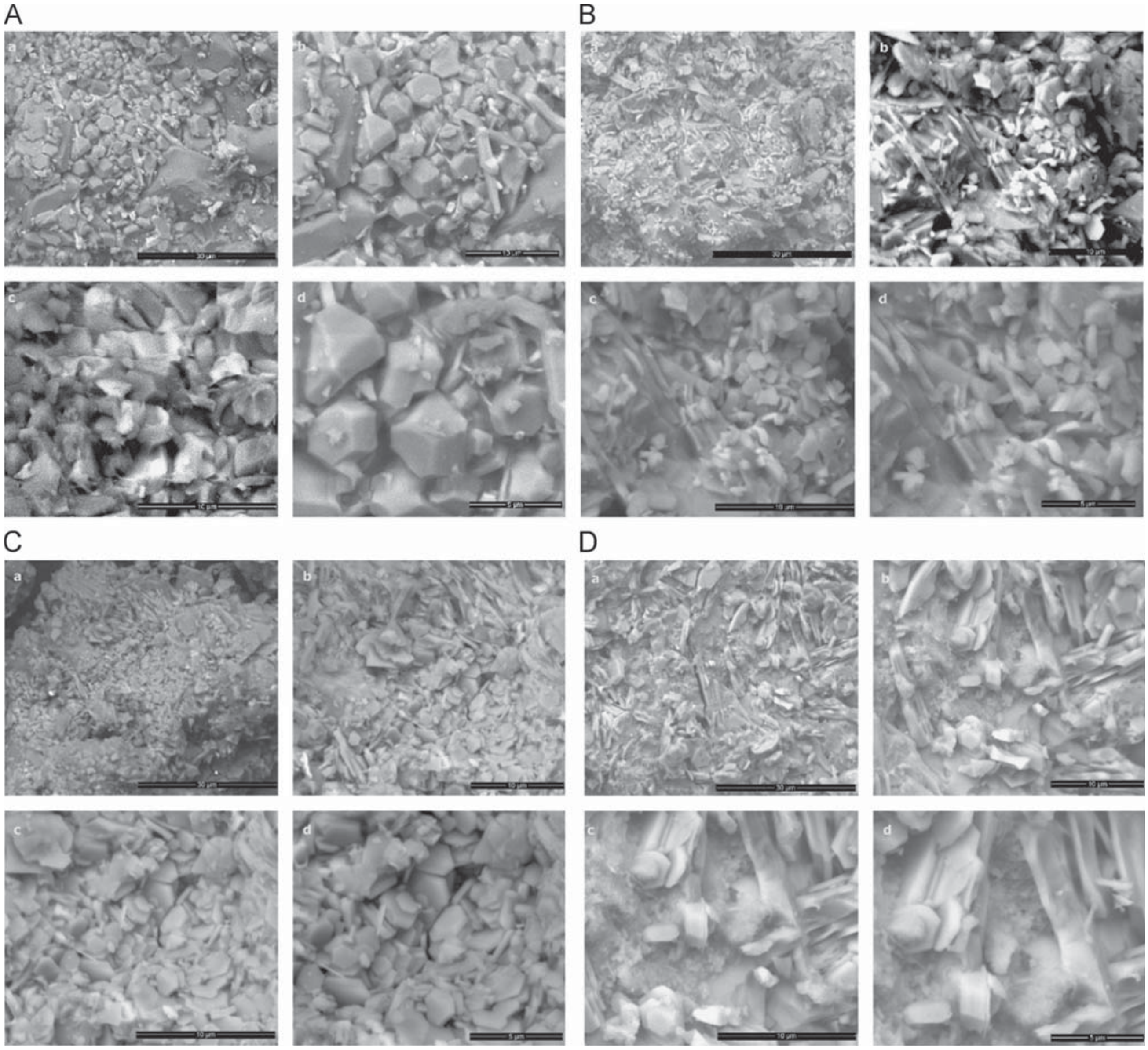

Fig. 11. (A) SEM of Q1 castable prepared with HAC80. (B) SEM of Q2 castable prepared with HAC80. (C) SEM of Q3 castable prepared with HAC80. (D) SEM of Q4 castable prepared with HAC80. (E) SEM of Q5 castable prepared with HAC80. (F) SEM of Q6 castable prepared with HAC80. (G) SEM of Q7 castable prepared with HAC80. (H) SEM of Q8 castable prepared with HAC80.

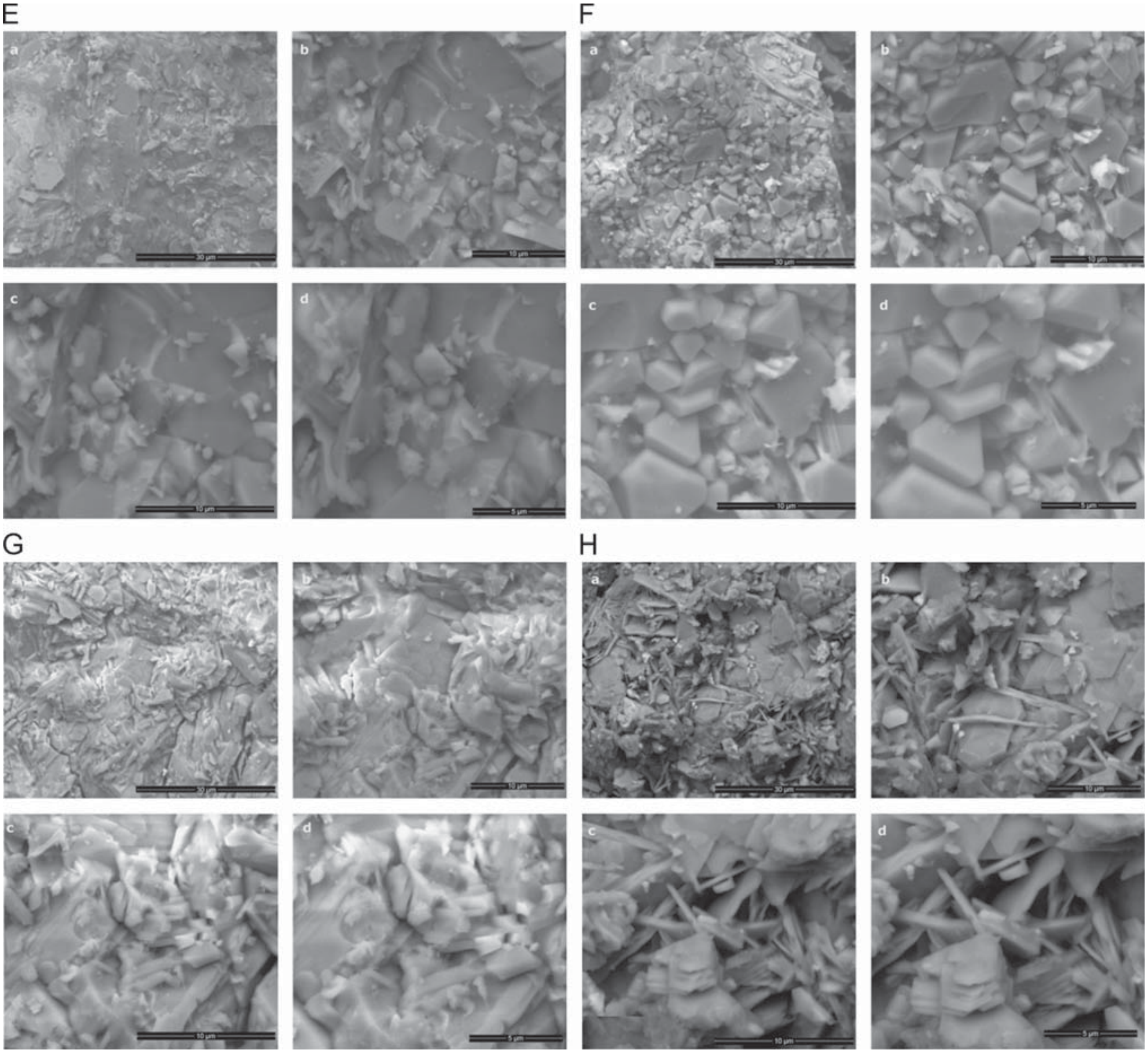

Fig. 11. (*continued*)

densification is not hampered. To conclude from this result, we may say that the safe range for these types of castables at higher loads is lower than 1600 °C. The impurities in the bauxite aggregate also increase the liquid phase sintering and decrease the porosity which consequently increases the mechanical properties.

3.9. SEM of Q1–Q8 castable

Backscattered images of bauxite based castables are given in Fig.11. The microstructural evolution of castables fired at 1550 °C was examined using field emission scanning electron microscopy of representative regions of fractured specimens. Fig. 11(A)–(H) depicts SEM photomicrographs of Q series castables after firing at 1550 °C for 3 h where a, b, c and d represent different magnifications. Only Q series castables were chosen for analysis through SEM as they represented superior thermo-mechanical and physical properties than P series castables. All figures show that all the examined samples have a dense crystalline structure with a high rate of grain growth of spinel as well as direct bonding of the same crystals. The presence of free corundum noticed in all microstructures may hinder the grain growth of round spinel crystals. The high alumina cements bonding phases which were traced in all six spinel-based compositions, occur in low amounts, mainly at the grain boundaries of spinel and corundum, so they practically do not reduce the refractoriness of the materials. On the other hand, in samples with MgO and Cr_2O_3 additives, the amount of low melting phases appears to be increasing slightly, but they still are encountered in low amounts. The incorporation of chromium in the spinel lattice helps to increase the rate of strong, direct contact between the crystals.

In Fig. 11(A) and (D) the matrix includes CA and some liquid phases. SEM photomicrographs in Fig. 11(B) and (C) exhibit densely packed microstructure with an abundant face centered cubic spinel grain of comparable sizes, embedded in the trigonal corundum matrix. As we proceed to micrograph Fig. 11(D)–(H), some acicular (needle-shaped) mullite beside corundum grains appeared in the microstructure. The presence of such in-situ formed phase had given interlocking in castables and reinforced the matrix confirming the high strength and refractory properties of castables. The photos show a very compact and dense microstructure in which the octahedral crystals of magnesium aluminate and magnesium chromite spinels are directly bonded either together or with rounded magnesia crystals. The rod like or elongated crystals characterizing [$MgO \cdot Al_2O_3 + MgO \cdot Cr_2O_3$] solid solution are observed which extended among the spinel–spinel or corundum-spinel crystals bonding them together. On the other hand, the impurities that were present in Chinese bauxite could be accounted for a low melting glassy phases, which tend to decrease the refractory properties and their microstructure may appear as partially diffused structure in some regions. This property is more evident when we zoom into the microstructures while moving a–d in each plot. The influence of trace impurities presented during the processing of ceramics is well known and exploited in the control of densification, grain growth and morphology during sintering. The ability to control microstructure is important for achieving desired properties.

4. Conclusion

There has been a lack of conclusive statements on the implementation of combustion synthesized high alumina cement as monoliths and their high temperature behavior. Our work shows that the combustion synthesis is reliable and can be successfully used to produce pure, crystalline calcium aluminates, with good compositional control of the powders produced. Desired cementing phases having high refractoriness identified as CA, CA_2, and $C_{12}A_7$ were formed at a low temperature with small crystallite size ranging 18–38 nm. These prepared cements have better physical and cementing properties than their commercial counterparts. One advantage of this process is to produce pure cementing phases and exclude silicates which are the cause behind eutectic formations in such cement bearing castables. These silicate phases decrease the refractoriness and the cement is not suitable for high temperature usage.

The XRD patterns of castables evolved new and pure phases of corundum and spinel. Castable samples prepared by HAC having 80% alumina have better properties than the HAC having 70% alumina. Trigonal corundum and cubic spinel formed at high temperature facilitate ceramic bonding which were termed responsible for increase in the CCS, CMOR. Pea sized grains of corundum helped to improve spalling resistance. Dispersion of in-situ formed spinel in fine grained alumina present as a part of castable matrix, promotes its ductile elongation at high temperature and this phenomenon is responsible for high hot strengths of castables. SEM represents dense microstructure of all the samples and glassy phase appearance is due to the impurities present in bauxite. These excellent properties of these castables enable their use in various refractory applications such as fabrication of steel, aluminum, copper, glass, cement, chemicals, and ceramics.

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An overview on High Alumina Cement as Castable bonding system

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Declaration

The Declaration of the authors for publication of Research Paper in The Indian Journal of Research Anvikshiki ISSN 0973-9777 Bi-monthly International Journal of all Research: We, *Vijay Kumar ,Abhinav Srivastava and V. K. Singh* the authors of the research paper entitled AN OVERVIEW ON HIGH ALUMINACEMENTASCASTABLE BONDING SYSTEM declare that , We take the responsibility of the content and material of our paper as We ourself have written it and also have read the manuscript of our paper carefully. Also, We hereby give our consent to publish our paper in Anvikshiki journal , This research paper is our original work and no part of it or it's similar version is published or has been sent for publication anywhere else.We authorise the Editorial Board of the Journal to modify and edit the manuscript. We also give our consent to the Editor of Anvikshiki Journal to own the copyright of our research paper.

Abstract

The term high alumina cements stands for a family of refractory cements for high performance application; the calcium aluminate cements (CAC) or high alumina cement (HAC). The hydraulic strength development is due to a water bonding reaction of the calcium aluminate minerals to water-resistant hydrate phases (not water dissolvable). It is cold bonding system. Alumina contents of high performance HAC equal or exceed 70%, and remaining CaO content. The difference in mineral constitution between HAC and Portland cement can be seen in the $CaO\text{-}Al_2O_3\text{-}SiO_2$ *Phase diagram. Portland cement occurs in the relatively high CaO region, with* C_2S *and* C_3S *as its main constituents. Calcium alumina cement on the other hand, occurs in a region with high* Al_2O_3 *(and low CaO and* SiO_2*), a factor that accounts for their higher melting point and used as refractory cement, where CA,* CA_2*,* CA_6*,* $C_{12}A_7$ *are the main constituents in high alumina cement.*

Keywords: High Alumina cement, Cementing behaviour, Hydration Kinetics, Castables

1. Introduction

The working life of high alumina cement in steelmaking and other ceramic industries is greatly dependent on the material's ability to withstand high temperatures without undergoing significant deformation and corrosion. Therefore, one of the approaches used throughout the latest decades to improve the performance of high alumina cement has been the reduction of the liquid content formed at elevated temperatures on high-alumina refractory castables. Low-melting point eutectic phases are often formed in these castables because of the

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in these castables because of the reaction between alumina, SiO_2, and CaO. Outstanding gains in refractoriness have been obtained through reduction of the amount of CaO, SiO_2 and increase the Al_2O_3 content in high-alumina cement[1].

2. Salient Features Of High Aluminate Cement

Calcium aluminate cements are cements consisting predominantly of hydraulic calcium aluminates. Alternative names are “aluminous cement”, “high-alumina cement” and “cimentfondu”. The main active constituent of calcium aluminate cements is mono-calcium aluminate ($CaAl_2O_4$) [2]. It usually contains other calcium aluminates as well as a number of less reactive phases deriving from impurities in the raw materials. Rather a wide range of compositions is encountered, depending on the application and the purity of aluminium source used [3].

Fremy in 1865 prepared various melt of lime and alumina and found them to possess good hydraulic properties and this was confirmed by Michaelis some years later.Schott in 1906 had published a memoir showing the high strength which were given by fused calcium aluminates. Spackman’s aluminate compounds were prepared by adding bauxite to high-alumina slags. A number of natural cements containing additions of Spackman’s calcium aluminates were marketed in the United States about the 1910 under the name of Alca natural cements, but their manufacture was later abandoned. A further study of high-high alumina cements was carried out by P.H.Bates at the U.S.A. Bureau of standards, the first results of which were published in 1921[4].

Bates prepared high-alumina cements by clinkering in a small (20-foot) rotary kiln and tested their properties in concrete. The high alumina cement ‘CA’ is the main mineralogical ingredient along with CA, C_2A, $C_{12}A_7$, $C_4A_3SO_4$, CA_6, Al_2O_3 etc.In high purity high alumina cement have the lower amount of impurities less fluxing agents and as a refractory properties better. So it is better to use high purity, high alumina cement as a binder. Depending up on the amount of impurities present in the HAC it is divided in three groups[5].

a. Low purity
b. Intermediate purity
c. High purity

TABLE 1 *Composition & service temperature for such cements*

Types of cement	Composition (% indicated oxide)					Temperature
	Al_2O_3	CaO	SiO_2	Fe_2O_3	$Ti0_2$	
Low purity	36-47	35-42	3.5-9	7-16	0.50	1425⁰C
Intermediatepurity	48-62	26-39	3.5-9	1-1.3	0.05	1650⁰C
High purity	70-80	18-26	0.0-0.5	0.1-0.2	—-	<1870⁰C

In high purity high alumina cement lower amount of impurities i.e. less fluxing agents and as refractory properties better. So it is better to use high purity, high alumina cement as a binder. Depending upon the rate of hydration of different phases, high alumina cement is divided into 3 groups[3].

TABLE 2 *The rate of hydration different phases in HAC*

Hydration rate	Low purity	Intermediate purity	High purity
Fast	CA CA_2 $C_{12}A_7$ C	CA CA_2 $C_{12}A_7$ C	CA CA_2 $C_{12}A_7$ C
Slow	C_2S	C_2S	-

	C_4AF	C_4AF	-
Non hydrating	CT	-	-
	A	A	-

Calcium aluminate cements (HACs) are the most important type of non-Portland or special cements. Even so, the volume used each year is only about one thousandth of that of Portland cement. As they are considerably more expensive (four to five times), it is therefore not economic to use them as a simple substitute for Portland cement. Instead their use is justified in cases where they bring special properties to a concrete or mortar, either as the main binder phase or as one component of a mixed binder phase[5].

3. Manufacture Of High Alumina Cement

The raw materials used for the manufacture of high-alumina cement are lime stone and bauxite. Although alumina is very widely distributed in nature, bauxite is the only suitable material available commercially on a scale adequate for cement production. Bauxite also forms the raw material for the manufacture of aluminium metal of alum and aluminium sulphate, and of certain types of refractories. The material used in Great Britain comes from France and Greece. During the last war, when bauxite was short, use was made of aluminium dross and the red mud from the Beyer process for production of alumina[5].

High alumina cement was originally manufactured in a water-cooled vertical furnace, open-hearth furnace arranged with vertical stack, Electrical furnace also used for the manufacture of high alumina cement for the small amount, and high-alumina cement is also produced by fusion is a rotary kiln of a type similar to that used in Portland cement manufacture.

For low iron content (<4 per cent Fe_2O_3)in high alumina cement, it has not been found possible to clinker the raw materials containing a low iron content that are used commercially. And fast very fast cooling markedly reduces the rates of strength development though not the ultimate strength. Experiments by Berl and Lobein showed that the strength tended to increase the more slowly the mix was cooled and the more completely crystalline the product[6].

A especially pure type of high alumina cement, white in color, is made in England, France and U.S.A. for use as a bonding agent for castable refractories for use at high temperatures. Alumina instead of bauxite is used as the raw material and the cement which contains 70-80 present Al_2O_3 is practically free from silica and iron oxide. The pure cement contains CA, CA_2, and Al_2O_3 and has a much higher melting temperature than ordinary high alumina cement. It is made by a sintering or clinkering process. Sulpho-aluminate cement made by grinding together high alumina cement and gypsum or anhydrite was patented by the Lafarge Company and worked for a time in French Indo – China. It apparently proved difficult to control its properties, and its manufacture was discontinued. Cement based on a mixture of high alumina cement, gypsum and hydrated tetra calcium aluminate is used in the U.S.S.R. as a shrinkage compensating cement studies on mixtures of high alumina cement and gypsum, dehydrated at 600 – 700^{0}C. Suggested that a cement of this type has a resistance to chemical attack similar to high alumina cement, but lower heat of hydration and that it does not suffer from loss in strength when cured at temperatures up to 50^{0}C. This type of cement is, is in fact, very similar to the supersulphated slag cements, for, in both, a major product of hydration is calcium sulpho-aluminate. This compound is stable up to about 50^{0}C but at higher temperature it loses water and at 75^{0}C there is a considerable loss in strength with super sulphated cement. It also does not appear possible to get the very high strengths at one day, which is characteristic of high alumina cement at ordinary temperatures, form its mixes with calcium sulphate. The high alumina cement made commercially has been classified by Robson into four types[7,5].

Setting behavior of clinker phases:

Fast setting phases : C_3A, $C_{12}A_7$
Moderate setting : CA
Slow setting : CA_2, C_4AF
Non setting : CA_6, Al_2O_3, C_2AS

CA (Mono calcium Aluminate)
- It is principal hydraulic compound.
- It gives high strength.
- Specific properties slow setting.
- M. P. = 1605^0C

CA_2 (Mono calcium Di-aluminate)
- Auxiliary Phase.
- M. P. - 1700 - 1790^0C.
- Low in strength.
- Slow setting.

$C_{12}A_7$(Mayenite)
- Short IST and FST.
- Hydrates and hardens quickly.
- M. P. - 1415 - 1495^0C.
- Gives Low Strength.

C_2AS (Gehlenite)
- Slow setting.
- Little tendency to hydrate.
- Undesirable phase.
- M. P. - 1590^0C

C_4AF (Tetra CaAlumino ferrite)
- No contribution to setting.
- No contribution to strength

4. Effecting Of Impurities During Clinker Firing

Silica, iron oxide, Titania and alkalis can affect the hydration and firing for example: high SiO_2 amounts in the high alumina cement CaO-Al_2O_3 raw mix lead to the formation of the non-hydratingGehlenite (C_2AS) phase during firing.

Types of high - alumina cement:

TABLE 3 *Types of high alumina cement*

Type	Color	Al_2O_3(%)	Fe_2O_3(%)	SiO_2(%)	CaO(%)	Source ofalumina
1	Grey	37-40	11-17	3-8	36-40	Red bauxite
2	Light grey	48-51	1-1.5	5-8	39-42	Red bauxite
3	Cream grey	51-60	1-2.5	3-6	30-40	White bauxite
4	White	72-80	0-0.5	0-0.5	17-27	Alumina

Properties of high - alumina cement:

- Rapid strength development, even at low temperature
- High temperature resistance/refractory performance
- Resistance to a wide range of chemically aggressive conditions

5. Hydration Of High – Alumina Cement

Both physical and chemical changes take place when water is added to the cement. The hydration converts to the anhydrous cement powder into various hydrated phases. The hydrated phases does under certain circumstances the most important product of normal hydration is Cao, Al_2O_3 $10H_20$ metastable 'Hexagonal' hydrates (CaH_{10}, or C_2AH_8) and they tend to transform into the 'Cubic' hydrate (C_3AH_6) only stable alumina Hydrate existing over a wide range of temperature. The pure calcium aluminates show no such behavior when treated with very limited amounts of water, and the solution curves remain similar to those obtained in the presence of large excess of water and their concentration in the solution increases as the water: cement ratio is decreased. Finally concluded that at low temperature the hydrated monocalcium aluminate was formed in high alumina cement pastes and that at about 20^{O}c the hydrated dicalcium aluminate and alumina gel appeared, while at higher temperatures transformation $3Cao.Al_2O_3.6H_2O$ occurred. The relative extent to which the mono and the dicalcium compounds appear is likely to be influenced by the alkali content the cement, since the presence of alkali considerably modifies the equilibrium in the system CaO- Al_2O_3-H_2O[8].

"The main hydration reaction in high alumina cement":

$$CaO.Al_2O_3.10H_2O$$

$$\Downarrow$$

$$2CaO.\ Al_2O_3.8H_2O + Al_2O_3\,(Aq.)$$

$$3CaO.\ Al_2O_36H_2O + Al_2O_3\ (Aq.)$$

This alumina gel on ageing gradually crystallizes as gibbsite ($Al_2O_3.3H_2O$). The extent to which CAH_{10} or C_2AH_8 predominate in the hydration products depends on the temperature and also the cement. If C_{12} A_7 is present in the cement the C_2AH_8 appears more freely, as hexagonal plates. If there is any exposure to carbon dioxide, hexagonal plates of $3CaO.Al_2O_3$, $HACO_3.11H_2O$ is also formed. The predominance of CAH_{10} increases as the temperature is decreased and at 15^0C or below the content of C_2AH_8 as reported by various investigators has usually been small. When pure CA is hydrated, the critical temperature above which C_2AH_8 formed is about 23^0C. However the amount of C_2AH_8 reported by different investigators form high alumina cement at temperatures between about 20^0C and 23^0C varies considerably. It may perhaps be influenced by the alkali content of the cement as well as by the C_{12} A_7 content. The di-calcium aluminate hydrate, with ferric oxide replacing part of the alumina, C_2 (AF) H_8 is also formed form the ferrite compound in the cement. There is also a tendency for more of the di-calcium aluminate hydrate to appear on ageing, either by conversion of CAH_{10} or form further hydration of the ferrite compound in the cement. At 25^{O}C and above the initial main hydration products are C_2AH_8 and hydrated alumina, and as the temperature is raises further, the isometric compound C_3AH_6 increasingly becomes the dominant product within days of weeks. At temperatures of 25^{O}C and upwards the isometric C_3AH_6 is formed from the ferrite in amounts increasing with time and temperature. The extent to which Al_2O_3 is replaced by Fe_2O_3 in the hydration product form high alumina cement is still uncertain. After one day the original anisotropic grains of the cement have largely disappeared and have been replaced by the gel together with the typical spherulitic growths of hexagonal plate groups and needles[9].

6. Effect Of Temperature On Hydrated High-alumina Cement

The high alumina cement cured at high temperatures or subsequently exposed to them in a mist state, has a reduced strength. This is closely connected with the change in the nature of the hydration products. The compounds CAH_{10} and C_2AH_8 produced at ordinary temperatures are metastable, and on prolonged ageing tend to change into the cubic compound $C_3\ AH_6$. At ordinary temperatures this change is very slow and may never occur in concretes kept dry, but it must be expected to occur, even though very slowly, in wet concretes. At high temperatures it occurs rapidly. Midgley has defined 'half conversion' as the state in which the quantity of C_3AH_6 is equal to that of CAH_{10} as determined by DTA. For neat cements, the time for half conversion was about a week at 50^{0}C, 100 days at 40^{0}C and estimated 20 years or so at 25^{0}C. A concrete cube stored in water for 27 years at 18^{0}C was found to be about half converted but samples from a 30 year old concrete pile extracted from the seabed showed little sings of conversion, the predominant compound still being CAH_{10}. The maximum temperature of the sea in the region concerned was about 18^{0}C. When high alumina cement is hydrated at relatively high temperatures, i.e. 35-45^{0}C, the cubic compound is rapidly formed and can readily be observed under the microscope when hydration takes place in excess water, and detected by X-rays in pastes of the consistence used in practice. Its presence is also indicated by the manner in which the hardened cement loses water on heating. Thus the compounded C_3AH_6 loses most of its water between 225^{0}C and 275^{0}C of wider temperature range. It is found that the loss occurring between these temperatures increases markedly in cement cured at higher temperatures, or subsequently exposed to such temperatures in a wet condition[10].

CA shows a fall in strength, parallel to that of high alumina cement, on curing at high temperatures, as indicated by the data in below table.

TABLE 4 *Compressive strength of HAC cured at high temperature*

Age	Compressive strength (lb./in^2)	
	Stored in water at 18^{0}C	Stored in water at 45^{0}C
1 day	8715	6425
7 day	10140	3415
28 day	10770	2450

The change from the less basic forms of the hydrated calcium aluminates to the cubic C_3AH_6 is thus closely associated with the marked loss in strength. There is much evidence, however that it is the volume change on conversion, rather than the mineralogical nature or morphology of the hydrates formed, that is responsible for the fall in strength. Unless there are compensating factors these volume changes make the converted cement much more porous than the original. As will be shown later, this development of porosity is partly compensated in mixes of low water: cement ratio by the continuing hydration of anhydrous cement. It has also been found that C_3AH_6 and AH_3 can give as high strength as CAH_{10} if the porosity is low, and that the increase in porosity on conversion decreases with to water cement ratio[11].

Applications

Because of their relatively high cost, calcium aluminate cements are used in a number of restricted areas.

- In construction concretes, rapid strength development is achieved, even at low temperatures.
- In construction concretes, high chemical resistance is possible.
- In refractory concretes, strength is maintained at high temperatures.
- As a component in blended cement formulations, various properties such as ultra-rapid strength
- Development and controlled expansion can be obtained[5].

7. Salient Features Of Castable Refractory

The hydraulic monolithic refractories (or) refractory castables are mixture of calcium aluminate cement (refractory cement) and suitably graded refractory aggregates. The cement in refractory castables reacts with water at room temperature and forms a strong solid mass. This is mostly used for quick furnace lining and repairing. A Refractory Castable may be macroscopically characterized as a structure consisting of large aggregates bonded together by a finer bond phase or matrix. Today's dense Castable systems have complex compositions comprised of the generic materials such as aggregates, fine reactive fillers like alumina and microsilica, calcium aluminate cement (HAC) and deflocculants. The entire system can be considered to be an independent system and the final characteristics are as a result of the sum of interactions of all. Depending on the specific type of refractory, the aggregate and matrix may be of similar or vastly different in chemical and physical properties. It is evident that almost infinite combinations exist when different aggregates, bonding matrices and particle size distributions for a particular type of Castable are considered. The relative proportion of the constituents, their chemistry and mineralogy influence the flow and refractory property of the castables. Conventional castables contain a high proportions (15-20%) refractory cement and water (8-15%). The presence of CaO associated with cement is detrimental to the refractory as it is a flux for alumina-silicate materials to form low melting phases[12].

Monolithic castables are replacing the traditional fired and shaped refractories at a much faster rate due to some inherent advantages mentioned before. The refractory aggregates serve an important role in determining the service temperature of castables. Packing density of castables can be improved by filling the voids between aggregates with micronized powdery materials. The commonly used superfine particles are microsilica, reactive alumina etc. which improve the performance of castables. Finer Cr_2O_3 was also used for this purpose but the refractory makers became aware of its environmental hazards. Various methods are employed in the placement of monolithic like ramming, casting, gunning, spraying etc. Ramming masses are used mostly in cold applications where proper consolidation of the material is important[13].

Low cement castables

The low moisture content can be achieved by lowering the percentage of bonding material cement in castables. Thus above concept of low moisture low cement castables is generated. Reduction of the cement about 5-8% without determinately effect on the strength can be achieved by the addition of fine grained refractory materials and a deflocculant for homogenous distribution of the cement and fine grain additive and reduce the mixing water needed. Packing density of the monolithic refractory can be increased. The commonly used superfine materials are silica sol, silica fume, alumina gel, Cr_2O_3, TiO_2.

Micro fine silica (0.15um dia) is used to get the monolithic refractory having the high mechanical strength, high erosion resistance, good thermal shock resistance and low shrinkage. When low cement castables using super fine silica powder are heated above 1350 – 1400^0C. Silica reacts with calcium aluminates of cement bond vitreous anorthite phase which cause the rapid decrease of hot MOR. This drop in hot strength above 14000c is independent of the type aggregate used.

One of the remedies of this problem is the replacing micro fine silica by micro fine Al_2O_3 or Cr_2O_3.The product Cr_2O_3 develops a very rigid high temperature above 1400^{0C} bond and it improve the hot strength and other physical properties .The added ultrafine silica powder forms a strong refractory phase mullite at 13000c. The formation of mullite increases the hot MOR at 1400^0C. However this hot strength drops rapidly as the CaO content increase but it solves the setting and hardening problem.

Low cement castables depending on two parameters

- Depends on CaO content
- Mullite content after firing

These two parameters not independent of each other and intensive research work has been carried out to select the bond system from the Al_2O_3,SiO_2,CaO phase diagram, to develop the maximum Mullite formation at high temperature and also maintain the proper cold setting and hardening[14,15].

Ultra-Low Cement Castable (ULCC)

This can be achieved by lowering the percentage of cement 4% and increasing the percentage of silica fumes max 10% added. This new type of castable is known as ultra-low cement castable (ULCC). Though ULCC has higher hot MOR value than LCC but these materials are very week in the green strength at low temperatures. So except for the blast furnace cast house application ultra-low cement castable is not use widely[1].

8. Conclusions

Conventional castables have long been associated with ease of application.At the first introduction of low cement and ultra-low cement castables, installation sensitivity was a drawback which discouraged many refractory installers and consumers. The current generation of LCC and ULCC products has significantly improved placement characteristics in comparison to the first generation products. Additionally, refractory installers have learned the techniques and sensitivities required for the use of these products.

Today, precautions are still necessary in the placement of formulations with reduced cement levels. Ease of installation has greatly improved with castables containing lower cement contents. Improvements may be attributed to the increased knowledge of themechanisms in the interdependence of the cement, fillers and additives. This knowledge has motivated the development of improved cements and fillers which meet the exacting demands and requirements forreduced cement formulations.Despite this knowledge,ULCC and no cement castables still tend to be more sensitive to installation parameters than conventional castables. Each castable type has its own specific characteristics which result in a unique trade off of between robustness and final performance. In the same context each castable type and each bond system have inherent characteristics that mean they do not all work equally well in all applications. A choice needs to be made application by application and it is dangerous to generalize.

The choice of calcium aluminate bondedcastables by refractory manufacturers hasgrown significantly in the past few years.Today, castables are selected both forultimate performance and ease of installationcoupled with reduced risk of installationfailure. The single biggest advantage of HAC for castables lies in its flexibility that allows a multitude of castable types and installation technologies to be developed. The basic properties of cold as well as hot cohesion can easily be achieved with calcium aluminate cement bonded systems. This is coupled with a choice of installation robustness versus installed characteristics and performance. No other bond system is able to offer such options.

The selection of calcium aluminate cement must be considered carefully in the quest to optimize performance and installation success. There must be a continuing evolution in the quality of the HAC characteristics to meet the exacting demands of the refractory formulations. For further progress to be made simultaneous development of the castable and the bond system is needed. These developments will surely fuel the growth of castables and their potential replacement for other types of Refractories.

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I hereby affirm that the information provided above is true and accurate.

Date: 09/09/2014

Vijay Kumar

Place: Varanasi

(Vijay Kumar)